The spectroscopic characterization of the methoxy radical. III. Rotationally resolved A 2 A 1 – X 2 E electronic and X 2 E submillimeter wave spectra of partially deuterated CH2DO and CHD2O radicals

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The spectroscopic characterization of the methoxy radical. III. Rotationally resolved $\tilde{A}^2 A_1 \rightarrow \tilde{X}^2 E$ electronic and $\tilde{X}^2 E$ submillimeter wave spectra of partially deuterated CH$_2$DO and CHD$_2$O radicals

Dmitry G. Melnik, Jinjun Liu, Ming-Wei Chen, Terry A. Miller, and Robert F. Curl

1Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
2Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77005, USA

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Rotationally resolved laser induced fluorescence and stimulated emission pumping $\tilde{A}^2 A_1 \rightarrow \tilde{X}^2 E$ spectra, along with pure rotational spectra in the 153–263 GHz region within the $E_{3/2}$ component of the ground state in asymmetrically deuterated methoxy radicals CH$_2$DO and CHD$_2$O have been observed. The combined data set allows for the direct measurement with high precision of the energy separation between the $E_{1/2}$ and $E_{3/2}$ components of the ground state and the energy separation between the parity stacks in the $E_{3/2}$ component of the ground state. The experimentally observed frequencies in both isotopologues are fit to an effective rotational Hamiltonian accounting for rotational and spin-rotational effects arising in a near-prolate asymmetric top molecule with dynamic Jahn-Teller distortion. Isotopic dependencies for the molecular parameters have been successfully implemented to aid the analysis of these very complex spectra. The analysis of the first and second order contributions to the effective values of molecular parameters has been extended to elucidate the physical significance of resulting molecular parameters. Comparisons of measured parameters, e.g., spin-orbit coupling, rotational and spin-rotation constants, are made among the 5 methoxy isotopologues for which data is now available. Comparisons of experimental results, including the derived geometric structure at both the $C_3v$ conical intersection and at the Jahn-Teller distorted minima, are made with quantum chemistry calculations. © 2011 American Institute of Physics. [doi:10.1063/1.3615724]

I. INTRODUCTION

Over the past few decades, the methoxy radical CH$_3$O has received close experimental and theoretical attention for a number of reasons. Alkoxy radicals have been shown to be important intermediates in combustion of hydrocarbon fuels and in tropospheric chemistry. Of all the alkoxy radicals methoxy holds a special place, as it is the simplest species in the family. Due to its relative simplicity, theoretical, and computational study of this radical at a fairly high level of detail is feasible. Moreover, its relatively high symmetry gives rise to intramolecular processes which are of fundamental scientific interest. The molecule belongs to the molecular symmetry (MS) group isomorphic to the $C_{3v}$ point group whose three-fold axis coincides with the C–O bond. The presence of an unpaired electron spin and a nonzero projection of electronic angular momentum on the symmetry axis results in a significant spin-orbit interaction. The double degeneracy of the ground electronic state, $\tilde{X}^2 E$, and the presence of degenerate vibrational modes result in the Jahn-Teller distortion of the molecule. The interplay between spin-orbit and Jahn-Teller interactions results in a complex pattern of vibronic levels and also affects the rotational structure. Methoxy serves as a prototype for similar vibronic effects which have been observed in similar systems such as CH$_3$S, CF$_3$S, CF$_3$O, in their ground $\tilde{X}^2 E$ state and CdCH$_3$, MgCH$_3$, ZnCH$_3$ (Ref. 14) in their $\tilde{A}^2 E$ excited state.

Methoxy is also a benchmark molecule for unimolecular dissociation dynamics and intramolecular vibrational redistribution. Temps and coworkers have shown that methoxy radical undergoes unimolecular decay,

$$\text{CH}_3\text{O} \rightarrow \text{H}_2\text{CO} + \text{H}, \quad (1)$$

with a dissociation threshold of 8200 cm$^{-1}$. The dissociation dynamics were studied using stimulated emission pumping (SEP) of the Frank-Condon favored C–O stretch mode, $v_3$. Unfortunately, this method does not favor observation of the Frank-Condon disfavored C–H stretching modes, which strongly correlate with the path of the reaction, Eq. (1), particularly, the antisymmetric C–H stretch $v_4$ in CH$_3$O. The assignment of the $v_4$ band in the dispersed fluorescence (DF) spectra remained uncertain until recently when a part of an infrared absorption spectrum observed near 2885 cm$^{-1}$ has been identified as a perpendicular sub-band of this vibrational mode. However, the analysis of the spectra in this region is still incomplete due to its complexity. One possible approach to the dissociation dynamics in methoxy is to produce a unique C–H stretch motion by asymmetric deuteration to form CHD$_2$O.

The study of asymmetrically substituted methoxy radicals is also important from spectroscopic and quantum chemical points of view, since it is small enough to completely

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a)Author to whom correspondence should be addressed. Electronic mail: miller.104@osu.edu.
resolve the rotational and spin structure of both microwave and electronic spectra, and a rather complete analysis has been reported for CH$_3$O, CH$_3$O, and CD$_3$O. Methoxy radicals with one or two deuterons have a nuclear symmetry corresponding to the MS group isomorphous with the C$_s$ rather than the C$_{1v}$ point group, and the Jahn-Teller effect transforms into a pseudo Jahn-Teller effect. Efforts have been made in only a few cases, e.g., cyclopentadienyl and methane cation to analyze the rotational spectra of an asymmetric isotopologue of a Jahn-Teller molecule. Asymmetrically substituted methoxy radicals are one such species for which a detailed spectra analysis is still manageable, but also represent significant complication from the previous studies due to the effects of spin interaction which are negligible in cyclopentadienyl and the methane cation.

It is evident that capturing the effects of Jahn-Teller distortion in a molecule with lowered nuclear symmetry requires developing a detailed model that describes the spectra in terms of quantities with clearly defined physical meaning, connected to the molecule’s geometric and electronic properties. We previously developed such a model and showed that the symmetry lowering results in a more complex effective rotational Hamiltonian than that for the symmetrically substituted radicals. Herein, we extend our previous development of the effective rotational and spin-rotational Hamiltonian to elucidate the physical interpretation of the effective molecular parameters. We also obtain isotopic relationships for the parameters of the effective rotational Hamiltonian which enable comparison of results from asymmetrically deuterated species with those of normal and perdeuterated isotopologues.

Experimentally the first spectroscopic study of the asymmetrically deuterated methoxy radicals, CHD$_2$O and CH$_2$DO, has been undertaken by Kalinovskiy, who reported the measurement and analysis of rotationally resolved laser induced fluorescence (LIF) spectra of a number of bands belonging to $\Delta^2A_1^+ - \tilde{X}^2$ electronic transition in CHD$_2$O and CH$_2$DO. We have extended this early data by taking higher resolution LIF spectra, and adding stimulated emission pumping (SEP) and pure rotational submillimeter wave absorption spectra of the asymmetrically substituted species. Although the doubly deuterated species constitutes the primary dynamical interest, a concurrent study of the singly deuterated methoxy belonging to the same MS group is desirable for better understanding of the processes defining the eigenvalue pattern in such radicals. We also report the extension of the computational package SPECVIEW (Ref. 28) to the analysis of the rotational structure of open shell asymmetric rotor molecules exhibiting a Jahn-Teller effect.

II. EXPERIMENTAL

The experimental setup for measuring LIF and SEP spectra was nearly identical to that used in the recent studies of CH$_3$O and CD$_3$O, therefore only a brief description is given here. Methoxy radicals are produced by photolysis of appropriately substituted methyl nitrite seeded in a carrier gas in a free-jet expansion. Two laser systems, moderate and high resolution, were used to obtain the spectra. In the moderate resolution system, the output of the Nd:YAG pumped dye laser (Sirah) was frequency-doubled using KDP-C crystal to generate UV radiation required to pump $\Delta^2A_1^+ - \tilde{X}^2$ transition of methoxy radical. This system was used for survey scans of the LIF spectra and as a pump for high-resolution SEP measurements. The linewidth of the output of this system was $\sim 0.15$ cm$^{-1}$ with a measurement accuracy $\sim 0.02$ cm$^{-1}$ (600 MHz).

In the high resolution system, the output of a CW dye laser (Coherent 899-29) was pulse-amplified by a dye amplifier (Lambda Physik, FL2003) and subsequently frequency doubled using a KDP-C crystal. This laser system was used for high resolution measurements of LIF spectra as well as a pump in survey SEP scans. This system allows one to achieve FWHM spectral resolution of $\sim 300$ MHz, limited by a combination of laser bandwidth, Doppler broadening and unresolved hyperfine structure. The center of spectral lines could be determined to $\sim 1/6$ of the linewidth. Using the Doppler-free absorption of I$_2$ and high-finesse etalon for frequency calibration, we estimate an absolute accuracy of $\sim 50$ MHz for the line center determination.

The submillimeter FASSST spectrometer which has been used to obtain the rotational spectra, has also been described in detail previously; however, several modifications were made to the previously existing setup. The spectra were obtained using the pulsed FASSST spectrometer utilizing a backward wave oscillator BWO-24, covering the range between 151 and 263 GHz. Briefly, a submillimeter wave beam of a rapidly tuned frequency is optically focused onto a pulsed supersonic jet and coupled to a liquid helium cooled InSb bolometer. A small portion of the radiation is fed into a thermally stabilized Fabry-Perot cavity to provide frequency markers used for relative frequency monitoring and real time synchronization. The signal produced by an InSb bolometer, properly amplified and conditioned, is recorded in 200–300 MHz data frames using 12-bit ADC converter (ADLink, model PCI-9812). For absolute frequency monitoring, and as a part of synchronization scheme, a reference cell containing OCS is inserted in the submillimeter beam. The spectra of methoxy radicals were obtained by alternately recording the absorption spectra with and without radicals present with subsequent subtraction of the latter from the former. This procedure allows the elimination of absorption features permanently present, e.g., baseline variations, OCS and precursor absorption transitions, etc.

In this work, methoxy radicals were produced in a DC electrical discharge in the supersonic jet, using an electrode assembly mounted on the top of the standard General Valve nozzle (Series 9), as shown in Fig. 1. The assembly consists of two coaxial electrodes separated by a 1 mm gap. To prevent line distortion due to a Stark effect from stray discharge electric fields, the downstream electrode is grounded and topped with an aluminum disc 6 inch in diameter. Two magnetic coils whose common axis is perpendicular both to the direction of the jet and the microwave beam are attached to the aluminum disc and are used for the purpose of spectral line identification using the Zeeman effect, as will be discussed later.
The upstream electrode, sandwiched between the insulator and the Teflon mount is kept floating at high voltage within the range of 0–2000 V. Our experiments showed that the methoxy signal was stronger if the floating electrode was held positive with respect to the grounded electrode. To prevent stray corona discharge on the metal surfaces at high voltages, the outer parts of these surfaces were insulated with Teflon tape. The discharge operates in a self-igniting mode, i.e., the voltage across the discharge gap was held constant, and ignition occurred with the opening of the valve and injection of the gas mixture.

We have used two different precursors to produce methoxy radicals. One method uses removal of the hydrogen from the OH group of methanol by fluorine atoms where 

\[
\text{MeOH} + F \rightarrow \text{MeO} + HF, \quad (2)
\]

where Me=CH₃, CH₂D, CHD₂, or CD₃. We have used SF₆ and CF₄ premixed in helium carrier gas as a source for the fluorine atoms generated in the discharge. Although the presence of fluorine in the discharge is reported to favor the formation of methoxy radicals, we found that the strength of the observed methoxy transitions from discharged gas mixtures with added fluorine atom precursor is nearly the same as without the fluorine precursor. Moreover, with the addition of trace amount of SF₆ (typically 3%), the discharge current dramatically dropped due to the large electron affinity of SF₆, which led in certain cases to quenching of the discharge. We suggest that methoxy radicals are primarily formed as a result of electron impact induced dissociation:

\[
\text{MeOH} + e \rightarrow \text{MeO} + e + H. \quad (3)
\]

During initial tests, the production of radicals was monitored by observing the intensity of the hyperfine doublet at 192 255.5 and 192 260.4 MHz ($J' = 7/2 \leftrightarrow J'' = 5/2, P'' = -1/2$) of CH₃O. A typical trace of this doublet is shown in Fig. 2. In the experiments, the He carrier gas (99.995% grade) at pressure of 25–30 psi was passed through a vessel containing liquid methanol at room temperature, yielding an 8% equilibrium concentration of methanol. The discharge was run at an ignition voltage of 800–850 V. An increase of ignition voltage above this value resulted in excessive soot formation in the discharge gap with a consequent discharge contraction and excessive spectral noise.

An alternative method for production of methoxy radicals utilized methyl nitrite MeONO as a precursor,

\[
\text{MeONO} + e \rightarrow \text{MeO} + e + NO, \quad (4)
\]

where again, an isotopologically appropriate precursor was used. In this case, helium at pressure 20–25 psi was bubbled through the liquid precursor held at 177 K (−96°C) in a bath of melting toluene. The saturated vapor pressure of CH₃ONO at this temperature equals 8 Torr, resulting in a 0.8% concentration of the precursor. All other experimental conditions were the same as in experiments with methanol. Under these conditions, the intensity of methoxy lines was approximately 1.5–2 times higher than with methanol as a precursor.

Under discharge conditions a number of species besides methoxy radicals are present in the jet and can give rise to spectroscopically observed features. These molecules include precursor fragments, reaction products of methoxy radicals (notably, two isotopologues of formaldehyde), as well as precursor molecules, in ground and vibrationally excited states. Absorption spectra of all possible species are not readily available. Therefore, a number of procedures have been utilized to ensure a proper identification of the observed transitions. First, since methoxy radicals are transient species, only transitions observed when the discharge was on were assigned to methoxy. Second, we assigned only lines that were observed with both precursors. Third, all features that met the first two criteria were checked against available spectroscopic databases, and all transitions corresponding within experimental accuracy (1 MHz) to known species were excluded.

Finally, we have used Zeeman modulation to exclude any features that did not exhibit paramagnetic properties. The
The effect of an applied magnetic field on the spectra is shown in Fig. 3. The variation of the observed intensity of the transitions in methoxy with magnitude of magnetic field can be explained as follows. Methoxy radicals in low rotational levels exhibit a magnetic moment of the order of one Bohr magneton. When a magnetic field is applied, the $M_F$ degeneracy is partially removed, resulting in line broadening with a reduction in peak intensity. To reduce baseline effects, improve signal-to-noise, and prevent saturation of the ADC input circuits, an electronic bandpass filter with a fairly narrow bandwidth is used. With the typical filter setting, Zeeman-broadened spectral features generate an electrical signal at a frequency near the edge or outside of the filter transmission band. Hence, such lines are suppressed by both line broadening and frequency rejection mechanisms. In many cases, the combined reduction of intensity is about an order of magnitude, and observable methoxy lines are nearly completely removed from the spectrum with a magnetic field of 12–16 Gauss.

The possibility of other paramagnetic species was also considered. For example, Endo et al. report observation of very weak HCO transitions in their methoxy spectra. However, a search for known HCO transitions originating from low-lying rotational states in the 173 GHz region produced no observable lines.

III. THEORY

A. Ground $\tilde{X}^2E$ electronic state

The groundwork for the analysis of rotationally resolved LIF spectra of asymmetrically substituted methoxy radicals has been laid by Kalinovsky. who used an effective rotational Hamiltonian (ERH) of the vibrationless level of the $\tilde{X}^2E$ state that included asymmetric rigid rotor (excluding Jahn-Teller distortion), spin-orbit and spin-rotational terms. Following earlier work and provides the appropriate isotopic relationships between the spectral parameters. In the following, we review and extend previously discussed theoretical developments and apply them to the analysis of the observed rotational structure of the vibrationless levels of the asymmetrically substituted isotopologues of methoxy.

1. Vibronic eigenfunctions and eigenvalues

Although our present spectra do not involve transitions between different vibronic levels of methoxy, it is important to consider the nature of the lowest energy vibronic eigenfunctions and eigenvalues. There is a long history of the study of the vibronic structure of Jahn-Teller active molecules, even including spin effects. However, the information is much sparser for such molecules with their symmetry lowered by isotopic substitution, and so we examine this vibronic structure in some detail, using the previous works on symmetric isotopologues as a guide. In particular, we build upon the earlier work of Longuet-Higgins, the somewhat later and more general work of the Heidelberg group, the work of Watson, the book of Bersuker and our earlier review. We also acknowledge a recent and particularly lucid overview of some of this material by Stanton.

The vibronic Hamiltonian for any molecule in field-free space can be written as

$$H_{\text{vib}} = H_{\text{e}}^0 + T_N + U(\mathbf{r}_e, \mathbf{R}),$$

(5)

where

$$H_{\text{e}}^0 = T_e + U(\mathbf{r}_e, \mathbf{0}),$$

(6)

and $T_e$ is electronic kinetic energy, $T_N$ is the part of nuclear kinetic energy associated with vibrational motion of the molecule (the nuclear kinetic energy associated with rotational and translational motion is ignored for the purpose of discussion of the vibronic problem), and $U(\mathbf{r}_e, \mathbf{R})$ is the total potential energy of the molecule written as a function of electronic coordinates, $\mathbf{r}_e$, and displacement, $\mathbf{R}$, along an appropriate set of the nuclear coordinates with respect to the reference configuration. The term $U(\mathbf{r}_e, \mathbf{0})$ in Eq. (6) is the total potential energy of the molecule at the reference $\mathbf{R} = \mathbf{0}$ configuration, which we take to be at the conical intersection.

It is therefore convenient to evaluate Hamiltonian Eq. (5) in a basis set which is a product of $\mathbf{R}$-independent electronic eigenfunctions and $\mathbf{R}$-dependent vibrational wavefunctions. The asymmetric isotopic substitution leaves the...
electronic Hamiltonian, Eq. (6), unchanged, therefore we use the same axially symmetric complex electronic basis functions \( \ket{e_+}, \ket{e_-} \), with the corresponding eigenvalues \( E_i^e = E_i^e = E_0^e \), as have previously been used\(^{20,21} \) for the analysis of the symmetric species. The \( \ket{e_{\pm}} \) electronic functions can be expressed as

\[
\ket{e_{\pm}} = 2^{-1/2}(\ket{e_+} + i\ket{e_-}),
\]

where we take \( \ket{e_+} \) and \( \ket{e_-} \) to be diabatic states which transform as \( A' \) and \( A'' \), respectively.

Equations (5) and (6) have the same general form for any choice of the nuclear coordinates \( \mathbf{R} \), as long as they form a complete basis in the \((3N-6)\) dimensional space. Therefore, we can recast these expressions in dimensionless nuclear coordinates, \( q \), and conjugate momenta \( p \), which are related to the mass-weighted normal coordinates, \( Q \), and momenta, \( P \), by

\[
q_k = \left( \frac{2\pi \omega_k}{\hbar} \right)^{1/2} Q_k, \\
p_k = \left( \frac{1}{2\pi \omega_k \hbar} \right)^{1/2} P_k,
\]

where \( \omega_k \) is the fundamental frequency of the \( k^{\text{th}} \) vibrational mode. With this choice of coordinates, the vibrational basis \( \ket{\mathbf{v}} \) can be represented as the product of one-dimensional harmonic oscillator eigenfunctions associated with the vibrational modes \( \ket{v_s}, \ estimated as \( \ket{v_t} \), transforming as the \( A' \) and \( A'' \) representations under exchange of the two identical hydrogen nuclei combined with inversion in the asymmetrically substituted methoxy. Hence, the primitive electronic-vibrational basis can be written as follows:

\[
\ket{e_{\pm}} \ket{\mathbf{v}} = \ket{e_{\pm}} \prod_{s \in A'} \ket{v_s} \prod_{t \in A''} \ket{v_t}.
\]

We now can expand the Hamiltonian in Eq. (5) in the power series in \( q \), which we truncate at the second order terms. This can be written as a matrix representation in the \( \ket{e_{\pm}} \) basis,

\[
H_v = H_v^0 + H_v^0 + H_{JT}^1 + H_{JT}^2,
\]

\[
H_v^0 = \frac{1}{2} \left( \sum_m \omega_m (p_m^2 + q_m^2) \right) \text{ and } H_v^0 = \left( \begin{array}{cc} E_0^e & 0 \\ 0 & E_0^e \end{array} \right),
\]

\[
H_{JT}^1 = \left( \begin{array}{cc} 0 & \sum_s k_s \omega_s q_s - i \sum_t k_t \omega_t q_t \\ \sum_t k_t \omega_t q_t + i \sum_s k_s \omega_s q_s & 0 \end{array} \right)\text{ and } H_{JT}^2 = \left( \begin{array}{cc} 0 & \sum_{ss'} b_{ss'} q_s q_{s'} \\ \sum_{ss'} b_{ss'} q_s q_{s'} - \sum_{tt'} b_{tt'} q_t q_{t'} - i \sum_{st} b_{st} q_s q_t & 0 \end{array} \right),
\]

where the index \( m \) runs over all vibrational modes, \( s \) runs over vibrational modes transforming as \( A' \) and \( t \) runs over \( A'' \) modes.

The following notation also has been introduced:

\[
\omega_m = \bra{e_{\pm}} \frac{\partial^2 U}{\partial q_m^2} \ket{e_{\pm}}_{q=0}, \\
k_s = \frac{1}{\omega_s} \bra{e_+} \frac{\partial U}{\partial q_s} \ket{e_-}_{q=0}, \\
k_t = \frac{i}{\omega_t} \bra{e_+} \frac{\partial U}{\partial q_t} \ket{e_-}_{q=0}, \\
b_{ss'} = \frac{1}{2} \bra{e_+} \left( \frac{\partial^2 U}{\partial q_s \partial q_{s'}} \right) \ket{e_-}_{q=0}, \\
b_{tt'} = -\frac{1}{2} \bra{e_+} \left( \frac{\partial^2 U}{\partial q_t \partial q_{t'}} \right) \ket{e_-}_{q=0}.
\]
coupling Hamiltonian which contains all terms that are second order in vibrational coordinates (conventionally referred to as quadratic Jahn-Teller, bilinear, and cross-quadratic coupling, respectively), excluding the harmonic potential terms of Eq. (10c).

For the rotational spectrum addressed in this paper, we need some knowledge about the eigenvalues and eigenfunctions of $H_{e\nu}$. The information required for its eigenvalues can be largely obtained by qualitative arguments concerning the vibrationless level, since the spectral observations are limited to the vibrationless level. If one neglects $H_{JT}^1 + H_{JT}^2$ then for the symmetrical methoxy, the zero point level is 2-fold degenerate (4-fold when electron spin is considered) with 6 distinct (3 doubly degenerate) vibrational frequencies contributing to the zero point energy (ZPE). It is well known that adding the Jahn-Teller terms will split degeneracies in higher vibrational levels but the vibronic Hamiltonian $H_{e\nu}$ retains 3-fold symmetry and the lowest vibronic level remains a degenerate E state.

However, while $H_{e\nu}$ possesses $C_{3v}$ (technically it has a molecular symmetry group isomorphic to $C_{3v}$) symmetry for symmetrical hydrogen isotopes, as written it only has symmetry isomorphic to $C_s$ corresponding to interchange of the pair of identical hydrogen nuclei combined with inversion. As written in Eq. (10) the symmetry of each $H_{e\nu}^0$, $H_{JT}^1$, and $H_{JT}^2$ likewise corresponds only to interchange of the pair of identical hydrogen nuclei combined with inversion. However, the effect of reducing the symmetry differs among the terms. For $H_{e\nu}^0$ the number of distinct $\omega_m$ increases from 6 to 9, but since the $\omega_m$ are the same for each the $|e_+\rangle$ and $|e_-\rangle$ basis functions no resolution of the vibronic degeneracy of the zero-point level occurs. This vibronic degeneracy can be removed by the addition of both $H_{JT}^1$, and $H_{JT}^2$. The resulting eigenfunctions are then of $\nu'$ and $\nu''$ symmetry and of course the overall vibronic energy level pattern is quite complex. However, if we restrict our attention only to the “vibrationless” components wherein the rotational structure was experimentally observed we can replicate the eigenvalues with a simple effective operator $\tilde{H}_Q$ where

$$\tilde{H}_Q = \frac{1}{2} \left( \begin{array}{cc} 0 & \Delta E \\ \Delta E & 0 \end{array} \right).$$

Since $H_{JT}^1$ and $H_{JT}^2$ only have off-diagonal matrix elements in the $|e_\pm\rangle$ basis, we use the above form with only off-diagonal terms. Obviously, it would be possible to replicate the splitting of the vibrationless level with a diagonal matrix with two unique elements; however, this would not give the proper form in this basis in which the spin-orbit interaction is diagonal (see Sec. III A 2).

While $\tilde{H}_Q$ is a part of the vibronic Hamiltonian, its magnitude is comparable to that of the spin-orbit interaction, which has traditionally been treated as a part of the effective rotational Hamiltonian. For a rotationless molecule its effect on the level structure is similar to that of spin-orbit interaction, although its effect on the rotational structure of spectra has been shown to be quite different. The reason for this, we will consider $\tilde{H}_Q$ as a part of the rotational Hamiltonian.

The final thing we need for analyzing the rotational spectrum are the eigenfunctions, $|e_{\nu\pm}\rangle$, of $H_{e\nu}$ so that we can calculate the appropriate matrix elements of the rotational Hamiltonian, $H_R$. Equivalently we can transform $H_R$ to an effective operator, $\tilde{H}_R$ in the original $|e_{\nu\pm}\rangle$ basis. We follow the lead of Watson who has shown how to apply this transformation (correct to $H_{JT}^2$) to the $H_R$. Specifically he defines a unitary transformation

$$S = e^{i\Theta},$$

such that

$$|e_{\nu\pm}\rangle = S'|e_{\pm}\rangle = e^{-i\Theta}|e_{\pm}\rangle |v\rangle.$$  

The Hermitian operator $\Theta$ is obtained straightforwardly from the expressions for $H_{e\nu}^0$ and $H_{JT}^1$ by the solution of the commutator equation

$$[\Theta, H_{e\nu}^0] = i H_{JT}^1$$

yielding

$$\Theta = -\left( \begin{array}{cc} 0 & \frac{1}{2} \sum_s k_s p_s - i \sum_t k_t p_t \\ \frac{1}{2} \sum_s k_s p_s + i \sum_t k_t p_t & 0 \end{array} \right).$$

2. The general form of the effective rotational Hamiltonian (ERH)

In this section, we will discuss the development of the ERH, $\tilde{H}_{ERH}$, using the results of Sec. III A 1. Since it will help to characterize various terms of $\tilde{H}_{ERH}$, it is useful to introduce the symmetrized rovibronic basis set that we will use to evaluate $\tilde{H}_{ERH}$,

$$|E, J, P, M, S, \Sigma, \varphi\rangle = \frac{1}{\sqrt{2}}\left[|e_{\nu+}\rangle|J, P, M\rangle|S, \Sigma\rangle + \varphi(-1)^J P + S - \Sigma|e_{\nu-}\rangle|J, -P, M\rangle \times |S, -\Sigma\rangle\right],$$

where $J = N + S$ is the total angular momentum of the molecule, $P$ is its projection on the molecule-fixed $z$-axis, $\varphi$ is the “parity” of the basis function with respect to the reflection in the plane of symmetry. The parameters of $\tilde{H}_{ERH}$ typically contain both first order, $X^1$, and second order electronic, $X^{2e}$, and vibrational, $X^{2r}$ contributions which have been discussed in previous works. The first order contribution to the parameters of $\tilde{H}_{ERH}$ can be viewed as expectation values of operators over the vibronic wavefunctions as derived in Sec. III A 1.

We can write the microscopic rotational Hamiltonian, including spin-rotational effects, as

$$H_R = H_{SO} + H_{ROT} + H_{SR}.$$  

We wish to obtain the first order contributions of the terms of $H_R$ to the effective rotation Hamiltonian, $\tilde{H}_{ERH}$, by taking expectation values over the vibronic basis functions, which can be realized by performing the transformation

$$\tilde{H}_R = e^{i\Theta} H_R e^{-i\Theta}.$$
where $H_Q$ is omitted from $H_R$ as it is already an effective operator. This transformation in Eq. (19) can be expanded in a Taylor series of which we will consider the lowest order nonvanishing terms,

$$
\tilde{H}_R = H_R + \frac{i}{2}[\hat{\mathcal{S}}, H_R] - \frac{1}{2} [\hat{\mathcal{S}}, [\hat{\mathcal{S}}, H_R]] + \ldots \tag{20}
$$

where the last term is an anticommutator.

As is shown in Appendix A, the substitution of the microscopic expressions for $H_{SO}$ into Eq. (20) produces

$$
\tilde{H}_{SO} = a \left( 1 - \sum_s k_s^2 - \sum_t k_t^2 \right) \mathcal{L}_z = a \sum_i \zeta_i d_H \mathcal{S}_z, \tag{21}
$$

where $\pm \zeta_i = \langle e_{\pm} | L_z | e_{\pm} \rangle$ and the vibronic projection operator $\mathcal{L}$ is introduced with components,

$$
\mathcal{L}_z^\pm = \langle ev_+ \rangle (ev_+) \pm \langle ev_- \rangle (ev_-) \tag{22}
$$

to define matrix elements in the twofold vibronic basis. The sum over $s$ runs over all modes that transform as $A'$ and the sum over $t$ runs over all modes that transform as $A''$. The factor $d_H$ corresponds in symmetric molecules to the Hamiltonian of a Jahn-Teller molecule was discussed on how the effective rotational and spin-rotational (see Sec. III A 4) Hamiltonian of a Jahn-Teller molecule was modified by asymmetric isotopic substitution. In this and Sec. III A 4, we shall follow the method of MLCM and apply the Watson transformation,36 which corresponds to simplifying a number of the following equations, we follow MLCM in introducing an operator $N = J - S$ to obtain an expression for $H_{ROT}$,

$$
H_{ROT} = \sum_{\alpha\beta} (N_\alpha - L_\alpha - G_\alpha) B_{\alpha\beta}(q)(N_\beta - L_\beta - G_\beta) \tag{25}
$$

In the final step of the analysis, the above definition for $N$ can be used to obtain operators dependent on $J$ as did MLCM.

The expansion of Eq. (25) produces terms bilinear in $N$, linear in $N$, and independent of rotational quantum numbers. The bilinear term generates the “pure” rotational part of the ERH, whereas the term linear in $N$ generates the Coriolis part of ERH. Ultimately the $X^1$ contributions to the rotational parameters are expressed as expectation values over the vibronic eigenfunctions, $\langle ev_{\pm} \rangle$. To accomplish this we follow the procedure of Watson36 and expand the rotational constant $B_{\alpha\beta}(q)$ in a power series in the vicinity of the reference configuration, $B_{0\alpha\beta}$, and truncate at the linear term. The reference configuration corresponds to the geometry at the conical intersection and is determined by equivalent bond lengths and angles for all isotopologues. Specifically we write

$$
B_{\alpha\beta}(q) = B_{\alpha\beta}^{\prime} + \sum_m \left( \frac{\partial B_{\alpha\beta}}{\partial q_m} \right)_{q=0} q_m. \tag{26}
$$

Inserting this expression for $B_{\alpha\beta}(q)$ into Eq. (25) for $H_{ROT}$ allows us to identify linear terms in $N$ which correspond to the effective Coriolis Hamiltonian, $\tilde{H}_{COR}$, and the bilinear terms that we assign to an effective, “purely” rotational Hamiltonian, $\tilde{H}_R$. We obtain an expression for $H_{COR}$,

$$
H_{COR} = - \sum_{\alpha\beta} B_{\alpha\beta}^{\prime} (L_\alpha + G_\alpha) N_\beta. \tag{27}
$$

Following MLCM and applying the Watson transformation,36 we write the effective Coriolis Hamiltonian in the $| ev_{\pm} \rangle$ basis,

$$
H_{COR} = -2B_{\alpha\beta}^{\prime} \zeta_i N_i \mathcal{L}_z^\pm - B_{\alpha\beta}^{\prime} \zeta_i (N_+ + N_-) \mathcal{L}_z^\pm, \tag{28}
$$

where the total vibronic angular momentum components are defined by

$$
\langle ev_{\pm} | L_z + G_z | ev_{\pm} \rangle = \pm \zeta_i, \tag{29}
$$

and we have utilized the vibronic projection $\mathcal{L}_z^\pm$ operator of Eq. (22).

Again following Watson,36 we apply the transformation in Eq. (16) to Eqs. (25) and (26) in order to obtain the expression for the effective $\tilde{H}_{ROT}$,

$$
\tilde{H}_{ROT} = \sum_{\alpha\beta} B_{\alpha\beta}^{\prime} \mathcal{L}_z^\pm + \sum_s k_s \omega_s C_s^{\alpha\beta} (\mathcal{L}_z^+ + \mathcal{L}_z^-) + \sum_i k_i \omega_i C_i^{\alpha\beta} (\mathcal{L}_z^+ - \mathcal{L}_z^-) \tag{30}
$$

where $R$ is the rotational angular momentum. The methoxy radical in its ground vibronic state also exhibits spin $S$, electronic $L$, and vibrational $G$ angular momenta, which are coupled together resulting in the total angular momentum $J$. In order to simplify a number of the following equations, we follow MLCM in introducing an operator $N = J - S$ to obtain an expression for $H_{ROT}$.
The quantities $C_{m}^{m \beta}$ ($m = s$ or $t$) in Eq. (30) are proportional to the derivative of the $B_{m}$ with respect to $q_{m}$:

$$C_{m}^{m \beta} = C_{m}^{m \alpha} \times \frac{1}{\omega_{m}} \left( \frac{\partial B_{m}}{\partial q_{m}} \right).$$

In case of symmetric isotopologues, the second term in Eq. (30) vanishes, and the sums over $s$ and $t$ are restricted to doubly degenerate modes $t$ with symmetric $t_{s}$ and antisymmetric $t_{i}$ components. For CH$_{3}$O and CD$_{3}$O, $C_{m}^{m \beta}$ quantities are not all independent and it has been shown\(^\text{11}\) that

$$\frac{\partial B_{xz}}{\partial q_{ta}} = - \left( \frac{\partial B_{xy}}{\partial q_{ta}} \right) = - \left( \frac{\partial B_{yx}}{\partial q_{ib}} \right),$$

$$\frac{\partial B_{xz}}{\partial q_{ta}} = \frac{\partial B_{yz}}{\partial q_{ta}},$$

$$\frac{\partial B_{zz}}{\partial q_{ta}} = 0.$$

As the nuclear symmetry of the molecule is reduced, generally, none of the equalities in Eq. (32) hold anymore. To obtain the functional form of $\tilde{H}_{\text{ROT}}$ for the asymmetrically substituted methoxy radicals, we expand the sum in Eq. (30) and treat all the derivatives in Eqs. (30)–(32) as independent. After regrouping the expansion terms and combining the results for the expression for the rigid-rotor rotational Hamiltonian for the IAS (Ref. 25), we obtain for $\tilde{H}_{\text{ROT}}$:

$$\tilde{H}_{\text{ROT}} = \left( \frac{B_{1x}^{1} + B_{1y}^{1}}{4} \right) \left( N_{+}^{1} N_{+}^{1} + B_{1z}^{1} N_{z}^{2} + \frac{B_{1x}^{1} - B_{1y}^{1}}{4} \right)$$

$$\times \left( N_{+}^{1} N_{+}^{1} + \frac{B_{1x}^{1} - B_{1y}^{1}}{2} [N_{+} + N_{-}, N_{z}]_{+} \right) \left( L_{z}^{2} + h_{1}L_{z}^{2} \right)$$

$$+ h_{1}L_{z}^{2} [N_{+}^{1} N_{z}^{2}] + h_{2}L_{z}^{2} [N_{+}^{1} N_{z}^{2}] + h_{3}L_{z}^{2} [N_{+}^{1} N_{z}^{2}] + h_{4}L_{z}^{2} [N_{+}^{1} N_{z}^{2}]$$

$$+ h_{5}L_{z}^{2} [N_{+}^{1} N_{z}^{2}] + h_{6}L_{z}^{2} [N_{+}^{1} N_{z}^{2}] + h_{A}N_{z}^{2}$$

$$\times \left( L_{z}^{2} + L_{z}^{2} \right) + h_{B} \left[ N_{+}^{1} N_{z}^{2} \right] \left( L_{z}^{2} + L_{z}^{2} \right),$$

where

$$B_{1x}^{1} = B_{1x}^{1} = B_{1x}^{1},$$

with the shorthand notation,

$$B_{m}^{1} = - \sum_{s} k_{s} \left( \frac{\partial B_{m}}{\partial q_{s}} \right),$$

$$B_{m}^{1} = - \sum_{t} k_{t} \left( \frac{\partial B_{m}}{\partial q_{t}} \right),$$

where the sums over $s$ and $t$ have the same restrictions as in Eq. (21). It is easily verified by direct substitution that if the values of the derivatives in Eq. (31) are restricted by Eq. (32), and $B_{xx}^{1} = B_{xx}^{1}$ and $B_{xx}^{1} = 0$, the coefficients $h_{1}, h_{2}, h_{A}, h_{B}$ vanish and Eq. (33) reduces to the well-known\(^\text{10,36,39}\) form of the rotational Hamiltonian for Jahn-Teller active symmetric top with two independent rotational constants $A = B_{zz}$ and $B = B_{xx} = B_{yy}$ and two terms, $h_{1}$ and $h_{2}$, describing the effects of Jahn-Teller distortion.

It can be shown (see Hirota et al.\(^\text{10}\) and Appendix B) that the terms in the lines 3–6 of Eq. (33) are diagonal in reflection parity quantum number, but the sign of the matrix elements of these terms depends on the reflection parity of the states involved. Hence, we will often refer to the terms of this nature (i.e., induced by the vibronic coupling) as “parity-dependent.” The sign of the matrix elements of the terms in the first two lines of Eq. (33) is the same for either parity, and therefore such terms will be called “parity-independent.” As the nuclear symmetry of the molecule is reduced from $C_{3v}$ to $C_{1v}$, two new parity-independent terms and four new parity-dependent terms are added to the $\tilde{H}_{R}$, as given in lines 2 and lines 4–6 respectively of Eq. (33).

To finalize the discussion of $\tilde{H}_{\text{ROT}}$ we consider the second-order contributions, $X^{2} = X^{(2c)} + X^{(2e)}$, to the effective rotational constants. It has been shown that in symmetric molecules,\(^\text{20,27}\) $B_{xz}$ receives a second order contribution $B_{xz}^{(2c)}$ due to interaction with electronically excited states, which is for practical purposes, negligible.\(^\text{20}\) Similarly we find that the $X^{(2c)}$ contribution for all the $B$ parameters in $\tilde{H}_{\text{ROT}}$ are negligible compared to the $X^{1}$ and $X^{(2e)}$ ones. In the symmetric molecule, $B_{xz}$ receives a more substantial contribution $B_{xz}^{(2e)}$ due to interaction with vibrationally excited levels of the ground electronic state. $\tilde{H}_{\text{ROT}}$ of the asymmetrically substituted molecule also contains two new parameters, $B_{xz}^{(1e)}, B_{xy}^{(1e)}$ and $B_{xz}^{(1e)}$, which likewise receive significant $X^{(2e)}$ contribution.

The expressions for the relevant $X^{(2e)}$ contributions are obtained following the line of the discussion of Liu et al.,\(^\text{27}\)

$$B_{xz}^{(2e)} = 4B_{zz}^{2} \sum_{n \neq 0} \frac{|\xi_{dn}B_{xz} + \eta_{dn}B_{xz}|^{2}}{E_{n} - E_{0}},$$

$$B_{xz}^{(2e)} = 4B_{zz}^{e} \sum_{n \neq 0} \frac{|\xi_{dn}B_{xz} + \eta_{dn}B_{xz}|^{2}}{E_{n} - E_{0}} = B_{xz}^{(2e)} B_{xz}^{(2e)},$$

$$B_{xz}^{(2e)} = 2B_{zz}^{2} \sum_{n \neq 0} \frac{|\xi_{dn}B_{xz} + \eta_{dn}B_{xz}|^{2}}{E_{n} - E_{0}} = \frac{1}{2} \left( B_{xz}^{(2e)} \right)^{2} B_{xz}^{(2e)},$$

$$B_{xz}^{(2e)} = 0,$$
and therefore the vibronic coupling always reduces the magnitude of both $B_{zz}$ and $B_{zz}$. $B_{zz}^{(2v)}$ is also negative, however, its magnitude is rather small and probably negligible. Eqs. (37) indicate that the second order vibrational contributions to the rotational constants are not independent and can be approximately related to each other through the values of $X^1$.

If we define

$$B_{ap}^{eff} = B_{ap}^{(1v)} + B_{ap}^{(2v)} + B_{ap}^{(2v)}$$

(38)

then the effective rotational Hamiltonian, $\tilde{H}_{\text{ROT}}$, can be obtained from Eq. (33) by replacing each $B_{ap}^{(1v)}$ term with $B_{ap}^{eff}$. The terms involving $h_1$ and $h_2$ of Eq. (33) can be reduced to the form of the sum of Eqs. (15) and (23) of MLCM by substituting $N = J - S$ and dropping constant terms. In Appendix B the terms involving $h_1$, $h_2$, $h_3$ and $h_4$ of Eq. (33) are reduced using the same substitution.

Unfortunately rigorous isotopic relationships between the $B_{ap}^{(2v)}$ parameters cannot be derived straightforwardly since the vibrational integrals on the right hand sides of Eq. (37) are isotopically dependent. In symmetrically substituted molecules, an isotopic dependence for the only significant vibrational contribution, $B_{zz}^{(2v)}$, has been satisfactorily estimated as

$$\left( B_{zz}^{(2v)} \right)^I = \left( \frac{B_{zz}^{(2v)}}{\tilde{\omega}_0} \right)^2 \left( \frac{\tilde{\omega}_I}{\tilde{\omega}_0} \right),$$

(39)

where the factor $B_I^I$ is introduced to account for the change of the energy gaps between the interacting vibronic levels,

$$B_I^I = \frac{\tilde{\omega}_I}{\tilde{\omega}_0}$$

(40)

The $\tilde{\omega}_0$ is the average vibrational frequency of the normal species and $\tilde{\omega}_I$ is the average vibrational frequency of the isotopologue of interest. Although Eq. (39) cannot be rigorously applied for asymmetrically substituted species, we will use it for the purpose of crude estimates in Sec. V.

The centrifugal distortion Hamiltonian $\tilde{H}_{CD}$ can also be taken as part of $\tilde{H}_{\text{ROT}}$. For symmetrically substituted species it is given by Endo and co-workers:\n
$$\tilde{H}_{CD} = \left\{ -D_N N^4 - D_{NK} N^2 \bar{N}_z^2 - D_K N^4 \right\} \bar{L}_z^2 + \frac{h_1 N}{2}$$

$$\times \left[ N_+^2 \bar{L}_+^2 + N_-^2 \bar{L}_-^2 \right]_+ + \frac{h_{12} N}{2} \left[ N_+^2 \bar{L}_+^2 + N_-^2 \bar{L}_-^2 \right]_+$$

$$+ \frac{h_{2N}}{2} \left[ N_+^2 \bar{L}_+^2 (N_+ N_+ + N_- N_-) + \bar{L}_+^2 (N_+ N_+ + N_- N_-) \right]_+$$

$$+ \frac{h_{2K}}{2} \left[ N_+^2 \bar{L}_+^2 + N_-^2 \bar{L}_-^2 \right]_+ + h_d (\bar{L}_+^2 N_+^2 + \bar{L}_-^2 N_-^2)$$

$$+ h_d (\bar{L}_+^2 N_+^2 + \bar{L}_-^2 N_-^2) + a_D \epsilon_{\alpha\alpha} a_d S_z N_+ \bar{L}_-^2$$

$$+ h_d (\bar{L}_+^2 N_+^2 + \bar{L}_-^2 N_-^2) + h_d \bar{L}_+^2 N_+ \bar{L}_-^2$$

(41)

The last three terms are centrifugal distortion terms for spin-orbit and Coriolis interaction. The centrifugal distortion Hamiltonian in Eq. (41) is derived for the symmetric top molecule. It can be shown that in the ERH of the symmetric top molecule set up in the IAS, additional CD terms will arise. However, since the angle between the $a$– and $z$–axes is small, such terms are expected to be small and their effect insignificantly for the rotational structure of the cold jet spectra. For the data limited to the transitions between levels with low rotational quantum numbers, some of the parameters in Eq. (41) cannot be determined independently and inclusion of additional centrifugal distortion terms would lead to unnecessary complication of the numerical analysis without real benefit. For similar reasons, we will not include higher order centrifugal distortion terms $H_{K_N}, H_{NK}, H_{D_N}, D_{Na}, D_{Nb}, D_{Ka}, D_{Kb}$ as well as any parity-dependent CD terms and fix $h_4 = 0$. Hence, in this work we will use the centrifugal distortion part of the ERH in the form of Eq. (41) with $h_4 = 0$. Even then the data will not prove sufficient to determine all these constants.

4. Spin-rotational Hamiltonian $H_{SR}$

The general form of the effective spin-rotational Hamiltonian is given by

$$\tilde{H}_{SR} = \frac{1}{2} \sum_{ap} \epsilon_{ap} [N_a, S_B]^+_n.$$  

(42)

The $X^1$ contributions to the values of $\epsilon_{ap}$ are well known to be small, and so the dominant contribution to these parameters comes from the interaction with the higher lying electronic states. Such an interaction can be expressed using second order perturbation theory:\n
$$\tilde{H}_{SR} = \sum_n \frac{\langle \psi_0 | H_{\text{COR}} | \psi_n \rangle \langle \psi_n | H_{\text{SO}} | \psi_0 \rangle}{\varepsilon_n - \varepsilon_0} + h.c.$$  

(43)

$H_{\text{COR}}$ and $H_{\text{SO}}$ are the microscopic Coriolis and spin-orbit Hamiltonian, and $|\psi_n\rangle$ run over all electronically excited states, and $|\psi_0\rangle, |\psi_0\rangle^\dagger$ are the components of the ground vibronic twofold, $|ev_{\pm}\rangle$ and $h.c.$ is the Hermitian conjugate. In the doubly degenerate vibronic state, there are two types of terms in $H_{SR}$,

$$\tilde{H}_{SR} = \tilde{H}_{SR}^0 + \tilde{H}_{SR}^1,$$  

(44)

in which $\tilde{H}_{SR}^0$ and $\tilde{H}_{SR}^1$ generate non-vanishing matrix elements diagonal in $|ev_{\pm}\rangle$ and between states of $|ev_+\rangle$ and $|ev_-\rangle$ respectively,

$$\tilde{H}_{SR}^0 = \sum_n \frac{\langle ev_{\pm} | H_{\text{COR}} | \psi_n \rangle \langle \psi_n | H_{\text{SO}} | ev_{\pm} \rangle}{\varepsilon_n - \varepsilon_0} + h.c.$$  

(45)

and

$$\tilde{H}_{SR}^1 = \sum_n \frac{\langle ev_{\pm} | H_{\text{COR}} | \psi_n \rangle \langle \psi_n | H_{\text{SO}} | ev_{\mp} \rangle}{\varepsilon_n - \varepsilon_0} + h.c.$$  

(46)

The terms of the both $\tilde{H}_{SR}^0$ and $\tilde{H}_{SR}^1$ can be derived explicitly from the expressions for the microscopic Coriolis, and spin-orbit Hamiltonian. Similarly to $\tilde{H}_{\text{ROT}}$, the reduction of nuclear symmetry from $C_{3v}$ to $C_2$ introduces new terms into the effective operator $\tilde{H}_{SR}^0$ and $\tilde{H}_{SR}^1$. $\tilde{H}_{SR}^0$ is the parity-independent part of spin-rotational Hamiltonian for IAS and has been discussed in detail previously, and we reproduce the resulting expression for $\tilde{H}_{SR}^0$,

$$\tilde{H}_{SR}^0 = \left\{ \varepsilon_{zz} N_z S_z + \left( \frac{\varepsilon_{xx} + \varepsilon_{yy}}{4} \right) (N_+ S_- + N_- S_+) \right\} \bar{L}_z^2$$
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\[
+ \left( \frac{\varepsilon_{xx} - \varepsilon_{yy}}{8} \right) (N_+ S_+ + S_+ N_+ + N_- S_- + S_- N_-) \\
+ \frac{\varepsilon_{zz}}{4} ((N_+ + N_-) S_z + S_z (N_+ + N_-)) \\
+ \frac{\varepsilon_{xz}}{4} (N_z (S_+ + S_-) + (S_+ + S_-) N_z) \right] \mathcal{L}^\dagger_z. \quad (47)
\]

If we make substitution of \(N = J - S\) into \(\hat{H}^0_{\text{SR}}\) we obtain the operator form of the sum of Eqs. (10) and (28) of MLCM.

The parity-dependent part \(\hat{H}^1_{\text{SR}}\) for symmetric species has been derived by Hougen.\(^{39}\) We use the same approach to derive its form, obtaining for \(\hat{H}^1_{\text{SR}}\) as follows:

\[
\hat{H}^1_{\text{SR}} = \varepsilon_1 (\mathcal{L}^2 N_+ S_+ + \mathcal{L}^2 N_- S_-) \\
+ \varepsilon_{2a} [\mathcal{L}^2 (N_z S_+ + S_- N_z)] \\
+ \varepsilon_{2b} [\mathcal{L}^2 (N_- S_+ + S_+ N_-)] \\
+ \varepsilon_{1a} (\mathcal{L}^2 + \mathcal{L}^2) N_z S_+ \\
+ \varepsilon_{1b} [\mathcal{L}^2 (S_+ N_+ + N_- S_+)] \\
+ \varepsilon_{1c} [\mathcal{L}^2 (N_+ S_+ + N_- S_-)] \\
+ \varepsilon_{1d} [\mathcal{L}^2 + \mathcal{L}^2] (N_+ + N_-) S_z \\
+ \varepsilon_{1e} [\mathcal{L}^2 (S_+ N_+ + S_- N_-)] \\
+ \varepsilon_{1f} [\mathcal{L}^2 (N_+ + N_-) S_z + (S_+ + S_-) N_z]. \quad (48)
\]

It should be noted that the \(C_1\) symmetry allows for 9 spin-rotational constants; however, only 8 terms result from the second order perturbation treatment indicated by Eq. (46). Some of these terms may still not be independently determinable,\(^{46}\) but can be obtained from the isotopic relationships for the parameters of symmetric isotopologues as shown in Sec. III A 5. If we make the substitution of \(N = J - S\) into \(\hat{H}^1_{\text{SR}}\), we obtain the operator form of Eq. (16) of MLCM for the unprimed terms. The primed terms are reduced by this substitution in Appendix B.

5. Spin-rotation isotopic relationships

The comparison of Eqs. (47) and (48) with the corresponding expressions\(^{10,39}\) for the \(\hat{H}^0_{\text{SR}}\) and \(\hat{H}^1_{\text{SR}}\) for symmetrical isotopologues shows that the reduction of symmetry from \(C_{3v}\) to \(C_1\) introduces three new parameters in \(\hat{H}^0_{\text{SR}}\) which appear in the last three lines of Eq. (47), and five new parameters in \(\hat{H}^1_{\text{SR}}\) appearing in the last six lines of Eq. (48), resulting in a fairly complicated functional form of the effective spin-rotational Hamiltonian. However, we will use the benefits of the IAS to show that most of the parameters in Eqs. (47) and (48) are not independent and can be expressed in terms of the components of the spin-rotational tensor of the symmetrically substituted species and components of the rotational tensors in both symmetrically and asymmetrically substituted radicals. These fundamental relationships were derived by Brown and co-workers:\(^{47}\)

\[
\sum \lambda_{ia} e_{\alpha i} = \sum \lambda_{iab} e_{\alpha b}, \quad (49)
\]

where the components of the inertial tensor \(I_{\alpha\beta}\) are related to the rotational tensor as

\[
I_{\alpha\beta} = \frac{\hbar^2}{2} (B^{-1})_{\alpha\beta}, \quad (50)
\]

and the starred values pertain to normal species. Eq. (49) is correct to second order in the values of \(e_{\alpha\beta}\) and based on the assumption that the second order spin-rotational constant is defined by Eq. (43) and therefore contains only the electronic contribution, \(e^{(2e)}_{\alpha\beta}\). It has been shown\(^{20,27}\) that the second order electronic contribution is by far the largest, so we can write for the parameters of the \(\hat{H}^0_{\text{SR}}\):

\[
\varepsilon_{xx} + \varepsilon_{yy} = \frac{B_{xx} + B_{yy}}{B^*} e^*_{bc}, \quad (51)
\]

\[
\varepsilon_{zz} = \frac{B_{zz}}{B^*} e^*_{bc}, \quad (52)
\]

\[
\varepsilon_{xx} - \varepsilon_{yy} = \frac{B_{xx} - B_{yy}}{B^*} e^*_{bc}, \quad (53)
\]

where the starred values correspond to normal isotopic species, \(\text{CH}_2\text{O}\).

It has been shown\(^{27,48}\) that the effective value of \(e_{\alpha\beta} = e^{(2e)}_{\alpha\beta}\) is dominated by the second order vibrational contribution, \(e^{(2v)}_{\alpha\beta}\). Using perturbation theory and results obtained by Liu and co-workers,\(^{27}\) we write the expressions for the only two vibrational contributions of significance,

\[
\varepsilon_{zz} = e^{(2v)}_{zz} = -4a B_{zz} \sum_{n \neq 0} \frac{d_{0n} \psi_{n 0}^* + \psi_{n 0} |d_{0n}|^2}{E_n - E_0}, \quad (54)
\]

\[
\varepsilon_{xz} = e^{(2v)}_{xz} = -4a B_{xz} \sum_{n \neq 0} \frac{d_{0n} \psi_{n 0}^* + \psi_{n 0} |d_{0n}|^2}{E_n - E_0} = \frac{B_{zz}}{B_{zz}^*} e^{(2v)}_{zz}, \quad (55)
\]

where \(d_{0n}\) and \(\psi_{n 0}\) were previously defined\(^{27}\) and the summation in Eqs. (54) and (55) runs over the vibrational levels of the ground electronic state. Since \(e_{zz}\) involves vibrational-type contributions and the vibrational structure is not presently well understood, a precise isotopologue relationship is not possible; however, an approximate one is suggested in Sec. V A 5.

Following Hougen\(^{39}\) but using the form of the \(H_{\text{COR}}\) and \(H_{\text{SO}}\), one can express the electronic contribution \(X^{(2e)}\) to the parameters of \(\hat{H}^1_{\text{SR}}\) in Eq. (48) in terms of quantities \(\Delta h_1\) and \(\Delta h_2\),

\[
\Delta h_1 = \frac{1}{4} (B_{xx} + B_{yy})^2 \\
\times \left\{ \sum_{i \in \mathcal{A}_2} \frac{|\langle \psi_i | L_z | \psi_0 \rangle|^2}{E_i - E_0} - \sum_{j \in \mathcal{A}_1} \frac{|\langle \psi_j | L_z | \psi_0 \rangle|^2}{E_j - E_0} \right\},
\]

\[
\Delta h_2 = B_{zz} (B_{xx} + B_{yy}) \sum_{i \in \mathcal{E}_z} \frac{|\langle \psi_i | L_z | \psi_0 \rangle|^2}{E_i - E_0}, \quad (56)
\]

where summations are performed over the excited electronic states of the appropriate symmetry. Since the electronic wavefunctions do not change upon isotopic substitution, we write...
for the $\varepsilon_1$, $\varepsilon_{2a}$, and $\varepsilon_{2b}$:

\[
\begin{align*}
\varepsilon_1 &= -\Delta h_1 \frac{2a_\perp}{B_{xx} + B_{yy}} = \frac{B_{xx} + B_{yy}}{2B^*} \varepsilon_{a*}, \\
\varepsilon_{2a} &= -\Delta h_2 \frac{a_\perp}{B_{xx} + B_{yy}} = \frac{B_{zz}^*}{A^*} \varepsilon_{2a}, \\
\varepsilon_{2b} &= -\Delta h_2 \frac{a_\parallel}{2B_{zz}} = \frac{B_{xx} + B_{yy}}{2B^*} \varepsilon_{2b},
\end{align*}
\]

where we have used $a_\parallel$ and $a_\perp$ notation of Hougen\textsuperscript{39} and the starred quantities pertain to the normal species. The remaining parameters in Eq. (48) are not present in the spin-rotational Hamiltonian of the symmetrical species, but they can be expressed as functions of other molecular parameters of the same isotopologue. We obtain, using second order perturbation theory and Eq. (56),

\[
\begin{align*}
\varepsilon_{1a}' &= -\Delta h_1 \frac{2a_\parallel}{B_{xx} + B_{yy}} = 2\varepsilon_{2a} \frac{B_{xx}}{B_{zz}}, \\
\varepsilon_{2a}' &= -\Delta h_2 \frac{a_\parallel}{B_{xx} + B_{yy}} = \frac{B_{zz}^*}{B_{xx} + B_{yy}}, \\
\varepsilon_{1b}' &= -\Delta h_1 \frac{a_\perp}{(B_{xx} + B_{yy})^2} = \frac{1}{2} \varepsilon_{2a} \frac{B_{zz}^*}{B_{xx} + B_{yy}}, \\
\varepsilon_{2b}' &= -\Delta h_2 \frac{a_\parallel}{2B_{zz}} = \frac{1}{2} \varepsilon_{2b}, \\
\varepsilon_{2b}'' &= -\Delta h_2 \frac{a_\parallel}{2B_{zz}(B_{xx} + B_{yy})} = \frac{1}{4} \varepsilon_{2a} \frac{B_{xx}}{B_{zz}}.
\end{align*}
\]

While Eqs. (57)–(64) contain the $a_\parallel$ and $a_\perp$ notation of Hougen, when making numerical estimates we shall adopt the approximation of Ref. 10 that $a_\parallel = a_\perp$. We finally note that the matrix elements that give rise to $d_{0n}$ and $g_{n0}^*$ in Eqs. (54) and (55) are diagonal in $|e_{a*}\rangle$ and therefore none of the parameters in $H_{SR}^1$ receives a second-order vibrational contribution.

**B. Excited $\tilde{A}^2 A_1$ electronic state and selection rules**

For the LIF spectra we also have to consider the rotational level structure of the excited $\tilde{A}^2 A_1$ state. The excited electronic state of methoxy radicals has been treated in detail in the Part I\textsuperscript{20} of these series. We note, that in this work we accessed the vibrational levels of $\tilde{A}^2 A_1$ electronic state with two quanta of excitation in $v_3$ mode and one quantum of excitation in $v_{6\alpha}$ mode, both of which have $a'$ vibrational symmetry in $C_s$ group. Hence it is appropriate to use the same ERH for the description of both of these states, and the one which was used for the analysis of $3^2$ level in symmetrically substituted species,

\[
\tilde{H}(\Lambda') = \tilde{H}_{\text{ROT}} + \tilde{H}_{\text{SR}},
\]

except that the $\tilde{H}_{\text{ROT}}$ is that of the asymmetric top. The Hamiltonian for the excited state is set up in principal axis system, hence, no off-diagonal components of the rotational tensor are present.

For the description of the rotational structure of the $\tilde{A}^2 A_1$ electronic state, the Hund’s case (b) basis $|J, N, K_a, K_c\rangle$ is the most convenient choice. However, for the convenience of calculation of the LIF and SEP transition intensities, the Hamiltonian has been set up in Hund’s case (a),

\[
|A, J, P, M, S, \varphi\rangle = \frac{1}{\sqrt{2}} |2A\rangle \left[ |J, P, M\rangle |S, \Sigma = \frac{1}{2}\right] + |(1-J)^{-p} |J, -P, M\rangle \times |S, \Sigma = -\frac{1}{2}\rangle,
\]

and the assignment of the rotational levels was then converted into Hund’s case (b) notation\textsuperscript{36,49}. We have used the same principles as were used before\textsuperscript{20,26,50} to derive the LIF and SEP transition intensities of the asymmetrically deuterated isotopologues. The detailed analysis is presented elsewhere\textsuperscript{26,50} hence only the final results are presented here.

The rovibronic eigenstates of the molecule in both ground and excited electronic states are linear combinations of the basis functions equations (17) and (66), respectively. Therefore, the line strength of the transition between the rovibronic level in the ground electronic state $i$ and rovibronic level in the excited state $j$ can be generally expressed as

\[
S_{ij} = 3 \sum_{m,m'} \sum_{n_\tilde{A},n_\tilde{X}} k_{i,j}^m k_{j,i}^{m'} \mu(n_\tilde{A}; n_\tilde{X})^2,
\]

in which $n_\tilde{A}$, $n_\tilde{X}$ are the basis functions equations (17) and (66), respectively, $k_{i,j}^m$ and $k_{j,i}^{m'}$ are the coefficients of expansion of the eigenstate in the corresponding basis sets, and $\mu(n_\tilde{A}; n_\tilde{X})$ is the electric dipole transition moment. The $k$-coefficients are obtained by the diagonalization of the effective rotational Hamiltonian matrix using the SPECVIEW computational package.\textsuperscript{28} Hence the task of the computation of the transition strengths is reduced to the calculation of individual transition moments $\mu(n_\tilde{A}; n_\tilde{X})$. Expanding the notation for the $n_\tilde{A}$, $n_\tilde{X}$, we write the expression for the transition moments as follows. For the LIF and SEP transitions involving the levels in $E_{1/2} (\Sigma = +1/2)$ component of the ground state:

\[
\mu(n_\tilde{X}; n_\tilde{A}) = \mu(2J', J, P, M, S, \Sigma, \varphi; 2a, J', P', M', S', \Sigma', \varphi')
\]

\[
= \sqrt{(2J + 1)(2J' + 1)} \left( \begin{array}{cc} J & 1 \\ -M & 0 \end{array} \right) M_J \delta_{J1/2} \delta_{\varphi,-\varphi},
\]

while for the transitions involving the levels in $E_{1/2} (\Sigma = -1/2)$ component of the ground state,

\[
\mu(n_\tilde{X}; n_\tilde{A}) = \mu(2J, J, P, M, S, \Sigma, \varphi; 2a, J', P', M', S', \Sigma', \varphi')
\]

\[
= \sqrt{(2J + 1)(2J' + 1)} \left( \begin{array}{cc} J & 1 \\ -M & 0 \end{array} \right) M_J \delta_{J-1/2} \delta_{\varphi,\varphi},
\]

where $M_J (q = -1, 0, 1)$ is the matrix element of the vibronic dipole moment.\textsuperscript{20}
Both isotopologues. For CH2DO, 65 rotational transitions involving the hyperfine structure and instrumental uncertainty both the uncertainties of the determination of the center of hyperfine components. The uncertainty of the measurement of lines was approximated as the center of mass of the observed not been analyzed. The rotational frequency of the observed

FIG. 4. Submillimeter wave traces of the rotational transitions of asymmetrically deuterated methoxy radicals. Left panel: \(|J = 2.5, P = -0.5, \Sigma = 0.5, -\rangle \rightarrow |J = 3.5, P = 0.5, \Sigma = 0.5, +\rangle \) transition in CH2DO, centered at 187 132.8 MHz. Right panel: \(|J = 2.5, P = 0.5, \Sigma = 0.5, -\rangle \rightarrow |J = 3.5, P = 0.5, \Sigma = 0.5, +\rangle \) transition in CHD2O centered at 178 996.3 MHz. Partially resolved hyperfine structure is seen in both traces.

The selection rules for the \(\vec{A}^2A_1 - \vec{X}^2E\) transitions are summarized as follows:

i. \(\varphi' = -\varphi\),
ii. \(J' = J, J \pm 1\),
iii. \(P' = \pm (P - 1)\) for \(M_+\) type transitions,
iv. \(P' = \pm P\) for \(M_0\) type transitions,
v. \(P' = \pm (P + 1)\) for \(M_-\) transitions,

where the “+” sign is for transitions involving the \(E_{3/2}\) component, and “−” is for \(E_{1/2}\) component. For the \(3_0^0\) band of both CH2DO and CHD2O, only \(M_+\) type transitions are allowed, whereas for \(6a_1^0\) band all types are allowed.

IV. EXPERIMENTAL RESULTS AND NUMERICAL ANALYSIS

A. Experimental results

The spectroscopy of the asymmetrically deuterated isotopologues of methoxy provides a variety of transitions involving the \(\vec{X}^2E_{3/2}\) component of the ground state. In the range of 154–263 GHz we have recorded and assigned 13 rotational transitions of CH2DO and 14 rotational transitions of CHD2O. Examples of the observed rotational lines of both isotopologues are shown in Fig. 4. Most of the observed transitions exhibit poorly resolved hyperfine structure which has not been analyzed. The rotational frequency of the observed lines was approximated as the center of mass of the observed hyperfine components. The uncertainty of the measurement of the center frequency is estimated to be 1 MHz, which includes both the uncertainties of the determination of the center of mass of the hyperfine structure and instrumental uncertainty due to the line shape distortion and variations of scan rate.

High resolution LIF spectra of the \(3_0^0\) and symmetric \((6a_1^0)\) vibronic bands of \(\vec{A}^2A_1 - \vec{X}^2E\) have been obtained for both isotopologues. For CH2DO, 65 rotational transitions belonging to the \(3_0^0\) band and 61 transitions belonging to the \((6a_1^0)\) have been observed and assigned. For CHD2O, we obtained 74 rotational transitions in the \(3_0^0\) band and 91 transitions in \((6a_1^0)\). The estimated uncertainty of the LIF measurements is 50 MHz. Example of LIF spectra for CH2DO are shown in Fig. 5.

SEP spectra of both isotopologues were obtained using strong rotational lines in the \(3_0^0\) band as pump transitions. A total of 8 transitions of CH2DO and 6 transitions of CHD2O were recorded with estimated uncertainties of \(\sim 70\) MHz. An example of a SEP spectra for CH2DO is shown in Fig. 6. The LIF and SEP spectra of CHD2O are of similar quality. The SEP transitions terminate on the upper \(2E_{1/2}\) fine structure component which is otherwise unaccessible in the free jet environment, and therefore complement the microwave and LIF data which only involve the thermally populated \(2E_{3/2}\) component.

In the global fit of the data to determine the parameters in the ERH, the observed microwave, LIF and SEP transitions were weighted inversely proportional to the square of the estimated accuracy of the transition frequency measurement, giving relative weight for the data types of 5000:2:1, respectively.

B. Data fitting and the parameter constraints

To fit the observed spectra data, the matrix of \(\vec{H}_{\text{ERH}}\) in the \(\vec{X}^2E\) ground state was constructed in the rovibronic basis, Eq. (17),

\[
\vec{H}_{\text{ERH}} = \vec{H}_{SO} + \vec{H}_{Q} + \vec{H}_{\text{COR}} + \vec{H}_{\text{ROT}}^0 + \vec{H}_{\text{ROT}}^1 + \vec{H}_{CD} + \vec{H}_{SR}^0 + \vec{H}_{SR}^1 \tag{70}
\]

where the terms on the RHS are given by Eqs. (21), (23), (27), (33), (41), (47), and (48). The required matrix elements are found in Refs. 10, 25, and Appendix B.

Figure 7 shows schematically how the terms of Eq. (70) shift and split the eigenvalues of \(\vec{H}_{\text{ERH}}\). On the far left (column 0) of the figure is the 8-fold degenerate state of a symmetric top without any interaction of the vibronic or spin angular momentum with the rotational angular momentum. Physically the degeneracy arises from the pairs of possibilities (parallel or anti-parallel) for the projections of the rotational, spin, and vibronic angular momentum. In
the basis set, \(|E, J, P, M, S, \Sigma, \varphi\rangle\) of Eq. (17), this corresponds to \(J = |P|\) (chosen to be 1/2) and the possible combinations of \(P = \pm J = \pm 1/2, \Sigma = \pm 1/2,\) and \(\varphi = \pm 1\).

Figure 7 introduces the terms of \(\hat{H}\) in a piece-wise fashion and shows how the basis functions evolve under \(\hat{H}\) to yield the eigenfunctions and eigenvalues. In column 1, \(\hat{H}_{\text{ROT}}\), which is the parity independent part of the rotational Hamiltonian, removes the degeneracy between the parallel and anti-parallel orientations of \(P\) and \(\Sigma\) as well as splitting the ± parallel components. The addition (column 2) of the parity independent Coriolis, spin-orbit and spin-rotation terms resolves the degeneracy of the anti-parallel \(P\) and \(\Sigma\) pair. The parity-dependent (column 3) terms of the rotational and spin-rotational Hamiltonians resolve the parity degeneracy of the \(P = \pm 1/2, \Sigma = \mp 1/2\) levels. The asymmetry of the top (column 4) is introduced for CHD2O and CHD2O which raises the parity degeneracy of the remaining states. In the far right (column 5) the shifting of the levels by the ZPE of the vibrations for the asymmetrically deuterated molecules is shown.

For the LIF experiments the Hamiltonian matrix elements for the \(A^2 \Pi_1\) state were also required. These are formally equivalent to those of the \(X\) state since a common \(\hat{H}\) to yield the eigenfunctions and eigenvalues. In column 1, \(\hat{H}_{\text{ROT}}\), which is the parity independent part of the rotational Hamiltonian, removes the degeneracy between the parallel and anti-parallel orientations of \(P\) and \(\Sigma\) as well as splitting the ± parallel components. The addition (column 2) of the parity independent Coriolis, spin-orbit and spin-rotation terms resolves the degeneracy of the anti-parallel \(P\) and \(\Sigma\) pair. The parity-dependent (column 3) terms of the rotational and spin-rotational Hamiltonians resolve the parity degeneracy of the \(P = \pm 1/2, \Sigma = \mp 1/2\) levels. The asymmetry of the top (column 4) is introduced for CHD2O and CHD2O which raises the parity degeneracy of the remaining states. In the far right (column 5) the shifting of the levels by the ZPE of the vibrations for the asymmetrically deuterated molecules is shown.

In Sec. III A, we have shown that with the reduction of nuclear symmetry the number of parameters in the ERH increases. At the same time, the available data sets for CHD2O and CHD2O, especially the submillimeter wave spectra, are neither as comprehensive nor as accurate as those available for symmetrically substituted species. Under these circumstances, in a least squares fit of the spectral data to the ERH, a number of the molecular parameters cannot be determined independently. However, entirely removing the corresponding terms from the ERH (or, equivalently, fixing their values at zero) would be physically unreasonable. Additionally, in the absence of the discriminating data some parameters can mimic the behavior of others, resulting in a large degree of correlation and subsequent instabilities in the convergence of the fit.

To minimize these problems, constraints can be applied to ensure relatively unambiguous and physically meaningful results from numerical fits. Certain parameters can be determined independently of the present data and fixed at a constant numerical value. We will refer to this kind of constraint as “static.” An example of such a constraint was fixing the value of centrifugal distortion parameter \(D_K\) in the analysis of CH2O [10,20] and CD3O [21] to the value of this parameter in the corresponding isotopologue of methyl fluoride.

Some other parameters of the ERH can be related to each other through well-established functional dependencies. These functional dependencies can reduce the number of independently varied parameters. For example, in the previous studies of symmetrically substituted species [10,20,21] the spin-rotational parameter \(\varepsilon_{2\sigma}\) was constrained to a ratio of \(B\varepsilon_{2\sigma}/A\).
with the three latter parameters being independently varied. We will call this type of constraint “dynamic.”

In Sec. III A, we have shown that most of the parameters of the effective spin-rotational Hamiltonian, \( \hat{H}_{SR} \), can be dynamically constrained and have derived the appropriate expressions for these constraints. The only exception is \( \epsilon_{zz} \) whose value depends on the vibrational structure of the asymmetrically substituted methoxy radicals, which is not available in sufficient detail given the sensitivity of the ERH to the value of \( \epsilon_{zz} \). Hence, \( \epsilon_{zz} \) is varied independently while all other parameters of \( \hat{H}_{SR} \) Eqs. (44), (47), and (48) are dynamically constrained using Eqs. (51)–(53), (55) and (57)–(64). We note that the ratios of \( \epsilon_{xx}/B_{zz} \), \( \epsilon_{xy}/(B_{xx} + B_{yy}) \) and \( \epsilon_{zz} \) are expected to be independent of the isotopic substitution. However, the comparison of these values in CH3O and CD3O shows a weak variation with isotopic substitution which we attribute to higher than second-order perturbations and correlation effects in the numerical fitting. In this work, the average values of these ratios in CH3O and CD3O were used to establish dynamic constraints for the spin-rotational parameters of ERH.

We also simplified the fitting for the centrifugal distortion (CD) terms, in \( \hat{H}_{CD} \), Eq. (41), which include parity-independent \( (D_K, D_{NK}, D_N) \) and parity-dependent \( (h_{1N}, h_{12N}, h_{2N}, h_{2K}, h_{4}) \) rotational terms, as well as spin-orbit \( (a_{D}\zeta, d) \), and Coriolis \( (\eta_\epsilon, \eta_K\zeta) \) centrifugal distortion terms. Zare used second order perturbation theory to account for the interactions with vibrationally excited levels, with the resulting values of CD parameters depending on the vibrational level structure. In CH3O and CD3O, we accounted for changes in vibrational structure by the introduction of \( \beta' \), see Eq. (39), with the parameter being derived under the assumption of near-uniform scaling of vibrational frequencies with isotopic substitution. While this assumption is valid for \( C_{3v} \) species, this is not necessarily a good assumption in asymmetrically substituted molecules due to asymmetry-induced mixing of \( v_1 \) and \( v_{1/2} \) modes, both transforming under the \( A' \) representation of the \( C_s \) point group. Hence \( \beta' \) cannot be used for formulation of parameter constraints to obtain accurate results, although, as we will show below, it can still be used for the purposes of rough estimates.

As an alternative, we have used CD parameters from a similar system, CH3F and its isotopologues to introduce static constraints. This method has been implemented by Endo et al. where \( D_K \) was statically constrained to its value in CH3F (Refs. 10 and 20) and CD3F respectively. Comparison of rotational CD parameters in symmetrically substituted isotopologues of CH3F (Refs. 51 and 52) with the corresponding experimental values in methoxy show that their ratio is nearly insensitive to the isotopic substitution. Therefore, we will extend this recipe to the analysis of asymmetrically...
substituted methoxy radicals by scaling the appropriate CD parameters of its fluorinated analogs by the average ratios of these parameters in symmetrically substituted species, e.g., $D_K(\text{CH}_2\text{DO}) = D_K(\text{CH}_2\text{DF})$, $D_{N K}(\text{CH}_2\text{DO}) = 1.79D_{N K}(\text{CH}_2\text{DF})$, $D_N(\text{CH}_2\text{DO}) = 1.25D_N(\text{CH}_2\text{DF})$, with similar relationships for $\text{CD}_2\text{O}$.

Our preliminary analysis, as well as prior work on symmetric species, showed that the calculated spectra are relatively weakly dependent upon the parity-dependent rotational centrifugal distortion parameters, as well as those for spin-orbit and Coriolis. Additionally, Coriolis CD terms show a rather unexpected trend by increasing their values from lighter to heavier isotopologue indicating that the physical interpretation of these parameters is rather obscure. Due to these results we constrained these parameters to their average values in the symmetric species. The higher order CD terms such as $h_4$ and $D_s$ were constrained to zero since the data in the present studies are limited to low $J$ levels whose energies are not strongly affected by the values of these parameters.

The excited state rotational structure has been fit to the ERH in the same general form as in case of symmetric methoxy radicals. As in the case of ground state, no modification to the $\tilde{H}_{\text{CD}}$ appeared to be necessary. For the purpose of consistency we dynamically constrained the centrifugal distortion constants to the corresponding values in the ground state. We have also found in the initial fits that both $e_{aa}$ and $e_{bb} - e_{cc}$ are very small and essentially undetermined, therefore these terms were excluded from the final analysis. These restrictions did not affect the quality of the fits.

A summary of the static and dynamic constraints used in this work is given in Table I. The results for the vibrationless level of the $\tilde{X}^2E$ state from the combined fit of microwave, LIF and SEP data of both isotologues to allowed transitions between the eigenvalues of the ERH are given in Table II with the numbers of the transitions used and the corresponding RMS for all the data types given at the bottom. The observed transitions of each spectral type were fit within experimental error. Corresponding results for the $\tilde{A}^2\Lambda$ state in the $3^2$ and $6^1$ vibrational levels are given in Tables III and IV. A summary of all observed spectral transition frequencies and the residuals between observed and predicted values using the fit parameters is available in the supplemental material.\footnote{53}

V. DISCUSSION

A. Ground $\tilde{X}^2E$ electronic state

In Secs. V A 1–V A 5, we will discuss the values of the parameters of the ERH for the vibrationless level of the ground $^2E$ state obtained from the numerical fits and their physical implications.

1. Asymmetry splitting $\Delta E$

The asymmetry parameter $\Delta E$ in the ERH results from the removal of the zero-point degeneracy caused by asymmetric substitution. In the earlier studies of the asymmetrically deuterated Jahn-Teller active molecules, such as cyclopentadienyl\footnote{22} it was found that the values of this parameter are nearly equal in magnitude and opposite in sign in the “counterpart” isotopologues (e.g., $\text{C}_4\text{H}_2\text{D}_2$ and $\text{C}_4\text{H}_2\text{D}$). Similar observations were made in studies of substituted benzenes\footnote{54} and earlier work on asymmetrically substituted methoxy radicals.\footnote{26} This propensity is supported by the experimentally measured values of $\Delta E$ as given in Table II.

Since the splitting is specific to the asymmetrically substituted species, unlike rotational and spin-rotational parameters, it is not possible to apply isotopic relationships to predict its value from the parameters of the symmetric species. However, previously there have been attempts to predict its value for the asymmetrically substituted cyclopentadienyl radical\footnote{55} and the methane cation\footnote{23} utilizing $ab\ initial$ calculations of the adiabatic potential energy surface (APES) of the lower sheet of the Jahn–Teller potential. These calculations are based upon the so-called isomer method, where the harmonic zero point energy (ZPE) is calculated for different positions of the isotope with respect to a symmetry element of the electronic eigenfunction. Conceptually there seem to be fundamental limitations to this approach. One of these limitations would be the neglect of kinetic coupling between the two sheets of the APES. Even considering only the lower sheet of the APES, one notes that it contains multiple minima separated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dynamic constraint</th>
<th>Static constraint</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_K$</td>
<td>$D_K^*$</td>
<td>$D_K^*$</td>
<td>10</td>
</tr>
<tr>
<td>$D_{N K}$</td>
<td>$D_{N K}^*$</td>
<td>$D_{N K}^*$</td>
<td>this work</td>
</tr>
<tr>
<td>$h_1$</td>
<td>$h_1$</td>
<td>$0.214$</td>
<td>this work</td>
</tr>
<tr>
<td>$h_1$</td>
<td>$h_1$</td>
<td>$2.8 \times 10^{-3}$</td>
<td>this work</td>
</tr>
<tr>
<td>$h_2$</td>
<td>$h_2$</td>
<td>$0.016$</td>
<td>this work</td>
</tr>
<tr>
<td>$(\eta_K, \zeta_1)^J$</td>
<td>$(\eta_K, \zeta_1)^J$</td>
<td>$0.529$</td>
<td>this work</td>
</tr>
<tr>
<td>$(\eta_K, \zeta_1)^J$</td>
<td>$(\eta_K, \zeta_1)^J$</td>
<td>$7.95$</td>
<td>this work</td>
</tr>
</tbody>
</table>

Table I. Summary of constraints on the parameters of the ground electronic state used in the fit. Superscript “T” denotes the asymmetrically substituted isotopologue and “H” denotes normal species. Numerical values of all statically constrained parameters are given in MHz. $D^{ij}$ indicate centrifugal distortion parameters of the corresponding CH$_3$F isotopologue.
In this section, we propose a rationalization for the agreement with the experimental observations of the approach. We then apply the approach to methoxy using several electronic structure calculations and compare these results with experiment.

The quantity $\Delta E$ is defined as the energy splitting of the vibronic eigenvalues from the electronic ground state. It is not so obvious how one calculates the lowest $A'$ vibronic level in the asymmetric species. It is not so obvious how one calculates the lowest $A'$ vibronic level in the asymmetric species. Equivalently $\Delta E$ is the separation between $e$ and $A'$ vibronic levels (derived from the adiabatic electronic structure calculation. To make that a dynamical constrained to other parameters as described in the text.

TABLE II. Ground electronic state molecular constants of CH$_2$DO and CHD$_2$O determined from fit. Values in parentheses are 1 $\sigma$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CH$_2$DO</th>
<th>CHD$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{zz}$</td>
<td>119043 (17)</td>
<td>94 871 (12)</td>
</tr>
<tr>
<td>$(B_{zz} + B_{yy})/2$</td>
<td>25 835 (5)</td>
<td>23 896 (5)</td>
</tr>
<tr>
<td>$(B_{yy} - B_{xy})/4$</td>
<td>431 (2)</td>
<td>-265 (3)</td>
</tr>
<tr>
<td>$B_{x}$</td>
<td>6370 (62)</td>
<td>-4518 (78)</td>
</tr>
<tr>
<td>$D_{K}$</td>
<td>1.38 b</td>
<td>0.74 b</td>
</tr>
<tr>
<td>$D_{NK}$</td>
<td>0.61 b</td>
<td>0.49 b</td>
</tr>
<tr>
<td>$D_{N}$</td>
<td>0.062 b</td>
<td>0.051 b</td>
</tr>
<tr>
<td>$a_{\xi_2 \eta_2}$</td>
<td>37 001 (20)</td>
<td>27640 (12)</td>
</tr>
<tr>
<td>$a_{\xi_1 \eta_1}$</td>
<td>0.529 b</td>
<td>0.529 b</td>
</tr>
<tr>
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<td>7.95 b</td>
<td>7.95 b</td>
</tr>
<tr>
<td>$a_{\tau}$</td>
<td>-1 789 347 (120)</td>
<td>-1 722 058 (90)</td>
</tr>
<tr>
<td>$a_{\tau_0}$</td>
<td>126 b</td>
<td>126 b</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>1 368 776 (156)</td>
<td>-1 302 406 (119)</td>
</tr>
<tr>
<td>$\epsilon_{zz}$</td>
<td>-31 655 (62)</td>
<td>-26 776 (39)</td>
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<td>-926 a</td>
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<td>10 a</td>
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<td>1275 a</td>
</tr>
<tr>
<td>$\epsilon_{yy}$</td>
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<td>175 a</td>
</tr>
<tr>
<td>$\epsilon_{1}$</td>
<td>163 a</td>
<td>150 a</td>
</tr>
<tr>
<td>$\epsilon_{2a}$</td>
<td>-386 a</td>
<td>-308 a</td>
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<td>$\epsilon_{2b}$</td>
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<td>-77 a</td>
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<td>$\epsilon_{r}$</td>
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<td>$\epsilon_{\tau}$</td>
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<td>-1221</td>
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<td>1.05·10$^{-3}$ b</td>
<td>1.05·10$^{-3}$ b</td>
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<td>2.8·10$^{-3}$ b</td>
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<tr>
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<td>0.106 b</td>
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<td>$h_{2}'$</td>
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<tr>
<td>$h_{A}$</td>
<td>-1007 (23)</td>
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</tr>
<tr>
<td>$h_{B}$</td>
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<td>-0.06</td>
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Data

<table>
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<tr>
<th>Transitions</th>
<th>$\sigma$, MHz</th>
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<td>MW</td>
<td>LIF, $3\epsilon_{0}^{2}$</td>
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<td>35</td>
<td>74</td>
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<tr>
<td>LIF, $6\epsilon_{0}^{2}$</td>
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<td>39</td>
<td>91</td>
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<tr>
<td>SEP, via $3\epsilon_{0}^{2}$</td>
<td>8</td>
<td>61</td>
<td>6</td>
<td>39</td>
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</table>

*Constrained to a constant value as described in the text.

**Dynamically constrained to other parameters as described in the text.

by low barriers around the Jahn-Teller moat. This is a situation for which a simple harmonic calculation of vibrational energy would not be expected to be at all accurate. Nonetheless previous ab initio calculations for substituted cyclopentadienyl radical and methane cation have shown rather good agreement with the experimental observations of $\Delta E$.

In this section, we propose a rationalization for the isomer method. In doing so, we believe that we have developed a somewhat different perspective and perhaps different interpretation of its application than has been previously described. Perhaps most important this rationalization provides guidance about the approximations and hence limitations of the approach. We then apply the approach to methoxy using several electronic structure calculations and compare these results with experiment.

The quantity $\Delta E$ is defined as the energy splitting of the doubly degenerate, $e$ vibronic level of methoxy by asymmetric deuteration. Equivalently $\Delta E$ is the separation between the lowest $A'$ and $A''$ vibronic levels (derived from the $e$ level) in the asymmetric species. It is not so obvious how one calculates the lowest $A'$ and $A''$ vibronic eigenvalues from an adiabatic electronic structure calculation. To make that
connection we note that to obtain the values of $\Delta E$ from \emph{ab initio} adiabatic calculations, we can return to the matrix of $H_{ev}$, Eq. (10), in the $|e_{\alpha}\rangle$ ($\alpha = x, y$) diabatic electronic basis. This basis set, transforming respectively as $A'$ and $A''$, then gives rise to a simple $2 \times 2$ matrix (see Eq. (3.5) of Ref. 34) which defines the APES as the eigenvalues of $H_{ev}$, with the condition that $T_{N} = 0$, which is a universal requirement for an adiabatic surface. The matrix elements of a general transformation $U$ which diagonalizes $H_{ev}$ can be expressed as

$$U_{11} = U_{22} = 2^{-1/2}(1 + d/W)^{1/2} \quad (71)$$

and

$$U_{12} = -U_{21} = 2^{-1/2}(1 - d/W)^{1/2}, \quad (72)$$

where $d$ denotes the diagonal matrix elements of $H_{ev}$ and $c$ its off-diagonal ones with $W = (d^2 + c^2)^{1/2}$.

When only linear Jahn-Teller terms are considered both Bierskude$^{56}$ and Koppel, et al.$^{34}$ show that the general form of $U$ reduces to

$$U_{11} = U_{22} = \cos(\phi'/2) \quad (73)$$

and

$$U_{12} = -U_{21} = -\sin(\phi'/2), \quad (74)$$

where $\phi'$ is the pseudo-rotation angle around the Jahn-Teller moat. (In this section, we use $\phi'$ for the pseudo-rotation angle of Refs. 34 and 56 since its phase convention differs from Watson’s$^{36}$ pseudo-rotation angle which we have previously denoted as $\phi$. The minima of the $|e_{\alpha}\rangle$ potential with $A'$ symmetry corresponds to $\phi = \pi$ or $\phi' = 0$ in the two conventions. Fortunately the result for $\Delta E$ (including sign) is invariant to these different phase conventions as can be seen by substituting $\phi' = -\pi$ into Eqs. (76)–(79).

The diabatic eigenfunctions $|e_{\alpha}\rangle$ ($\alpha = x, y$) are then related to the adiabatic eigenfunctions $|e_i\rangle$, $i = 1, 2$, by

$$\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = U^{-1} \begin{pmatrix} e_x \\ e_y \end{pmatrix} = \begin{pmatrix} \cos \frac{\phi'}{2} & -\sin \frac{\phi'}{2} \\ \sin \frac{\phi'}{2} & \cos \frac{\phi'}{2} \end{pmatrix} \begin{pmatrix} e_x \\ e_y \end{pmatrix}. \quad (75)$$

The function $\langle e_1, v = 0 \rangle H_{ev}^0 |e_1, v = 0 \rangle = \left( \cos \frac{\phi'}{2} \langle e_{vx} \rangle - \sin \frac{\phi'}{2} \langle e_{vy} \rangle \right)$

$$\cos^2 \left( \frac{\phi'}{2} \right) \langle E_x \rangle + \sin^2 \left( \frac{\phi'}{2} \right) \langle E_y \rangle, \quad (76)$$

where $H_{ev}^0$ is of the form of Eq. (10c), but with the normal coordinates and corresponding frequencies defined via the force constants of the APES. Clearly this step will limit the accuracy of the ZPE to the harmonic approximation and ignores any effect of the upper sheet of the APES.

For only a linear Jahn-Teller effect the energy around the moat on the lower sheet of the APES is independent of $\phi'$ and corresponds to a global minimum. If this were actually the case for methoxy one could calculate the ZPE at $\phi' = 0$ for the $A'$ level, denoted as $E_x$, and at $\pi$ for the $A''$ level denoted as $E_y$, and thereby obtain $\Delta E$ trivially from their difference. However, methoxy has a small quadratic Jahn-Teller effect so the moat of the APES is not exactly flat; rather it has saddle points at $\phi' = \pi$ and $\pm \pi/3$ and minima at 0 and $\pm 2\pi/3$. The saddlepoint at $\phi' = \pi$ prevents the calculation of a ZPE there from the \emph{ab initio} electronic structure calculation. Nonetheless, we can write at $\phi' = 0$,

$$\text{ZPE}|_{\phi' = 0} = E_x, \quad (77)$$

and at $\phi' = \pm 2\pi/3$

$$\text{ZPE}|_{\phi' = \pm 2\pi/3} = \frac{1}{4}(E_x + 3/4)(E_y). \quad (78)$$

Finally,

$$\text{ZPE}|_{\phi' = 0} - \text{ZPE}|_{\phi' = \pm 2\pi/3} = \frac{3}{4}(E_x - E_y) = \frac{3}{4}\Delta E. \quad (79)$$
FIG. 8. Different Jahn-Teller configurations of asymmetrically deuterated methoxy with their pseudo-rotation angles $\phi$ indicated. C and O are omitted. The light balls (1) represent the odd isotope of hydrogen, while the dark ones (2 and 3) represent the two common isotopes. In the square is the undis- torted configuration. In the circles are the Jahn-Teller minima. In the triangles (2 and 3) represent the two common isotopes. In the square is the undis- torted. The light balls (1) represent the odd isotope of hydrogen, while the dark

The $\Delta E$ can be calculated at the 3 minima on the APES at most angles of $\phi = 0, \pm 2\pi /3$. To determine $\Delta E$, we note that pseudo-rotation of $\phi = \mp 2\pi /3$ corresponds to a cyclic permutation (123) or (321) of the hydrogen atoms, a symmetry operation of the MS group. (Strictly true for the symmetric isotopologue only but since we are interested in the symmetry properties of the invariant APES, it suffices). As Fig. 8 shows this is equivalent to calculating the ZPE when the odd hydrogen isotope is in the (electronic) symmetry plane ($\phi = 0$) or one of the two common isotopes is in the symmetry plane ($\phi = \pm 2\pi /3$). The Jahn-Teller distorted geometries (minima and barriers) of methoxy were optimized at different levels of theory using the GAUSSIAN 09 package. The reaction path for pseudo-rotation has been verified by the Synchronous Transit-Guided Quasi-Newton (STQN) calculations. Hydrogen isotopes (H and D) were permuted between the three positions (see Fig. 9) and the ZPE for each configuration of a given isotopologue was calculated. The difference between the ZPEs of configuration 1 and configurations 3 or 5 scaled by 4/3 (see Eq. (79)) give a calculated $\Delta E$. The results are listed in Table V and compared to the experimentally determined values.

As Table V shows the calculations certainly give reasonably good predictions for $\Delta E$ considering the fact that the absolute values of the ZPE are of the order of thousands of wavenumbers. Only the HF calculation gives a clearly aberrant value, and frankly its prediction is expected to be of poor quality. The capability of the other calculations to obtain such a small numerical value of the ZPE with reasonable accuracy is largely attributed to the fact that in obtaining $\Delta E$, one calculates the difference of vibrational frequencies between configurations with the same geometry and force field and which differ only in the position of the odd hydrogen atom. Therefore many systematic errors in calculating the ZPE likely cancel out.

Nonetheless questions concerning the underlying premises of the use of harmonic frequencies from a APES remain to be addressed. With respect to the harmonic assumption it is worth noting that all 9 vibrational frequencies of the molecule contribute to the calculated $\Delta E$ and most of them are relatively high frequency and may be reasonably well approximated by the harmonic calculation. Moreover the same neglect of anharmonicity occurs for both the $A'$ and $A''$ states and so again the differences in the smaller anharmonic contributions may not make too much of an effect. There will of course be at least one normal mode with a major contribution from the low frequency motion around the Jahn-Teller moat, which we would expect to be poorly calculated in the harmonic approximation. Nonetheless, it is just one mode of 9, and since the mode itself will be of relatively low frequency apparently it may not distort the overall $\Delta E$ calculation greatly.

Finally there is the issue of kinetic coupling between the upper and lower sheets, which this calculation completely neglects since it is based only upon the lower APES. The wave packet calculations of Nagerb and Sibert apparently show that this coupling is clearly present. Since our calculation completely neglects it, we can only suggest that perhaps this coupling shifts the ZPE of both the $A'$ and $A''$ states comparably and therefore does not strongly alter $\Delta E$.

Nonetheless given the obvious approximations we consider the apparent ability of the simple ab initio harmonic calculation of the ZPE, to mimic experiment not fully understandable on theoretical grounds. We are presently pursuing the analysis of a dispersed fluorescence spectra of the asymmetrically deuterated methoxy that we have previously obtained. Hopefully this analysis and the comparison with results with electronic structure calculations will further clarify this matter.

2. Spin-orbit $a_{\zeta}d$ and Coriolis $B_{2\zeta}$

In the series of methoxy isotopologues, both the spin-orbit coupling constant $a$ and the expectation value of the projection $\zeta$ of the electronic angular momentum on the $z$ axis remain essentially the same since they both depend only on the electronic eigenfunction. However, the observed value of the spin-orbit splitting does change as it is affected by the Ham quenching factor $d_H$, Eq. (21), which indicates the degree of mixing of the electronic eigenstates due to vibronic coupling and depends on the vibrational structure of the molecule. All things being equal the degree of mixing tends to increase as the vibronic levels get closer together. The fundamental frequencies of the Jahn-teller active modes are reduced in the heavier isotopologues, thus reducing the value of $d_H$. Therefore, we expect the value of $a_{\zeta}d$ to monotonically

<table>
<thead>
<tr>
<th>Expt.</th>
<th>B3LYP</th>
<th>CCSD</th>
<th>MP2</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$(CH$_3$DO)</td>
<td>45.66</td>
<td>54</td>
<td>39</td>
<td>33</td>
</tr>
<tr>
<td>$\Delta E$(CH$_D$$_3$O)</td>
<td>-43.44</td>
<td>56</td>
<td>34</td>
<td>34</td>
</tr>
</tbody>
</table>

TABLE V. Comparison of $\Delta E$ (in cm$^{-1}$), derived from the experimental data and from quantum chemistry calculations. Basis set 6-31+G(d) is used in all calculations.
decrease from the CH$_3$O to CD$_3$O, which is observed experimentally (see Table II and the previous work$^{[20,21]}$ and as shown in Fig. 9 (red circles). The clear trend is a small, nearly linear decrease of $\zeta_d d_H$ with the number of deuterons, independent of the symmetry of the isotopologue.

Since $B_{zz}$ and $B_{xx} \zeta_1$ are measured independently experimentally (see Table II), a value of the Coriolis parameter $\zeta_1$ can be determined. The $\zeta_1$ is a combination of the effective projection of the electronic angular momentum along the $z$ axis, $\zeta_d d_H$, and the expectation value of the projection $\ell_z$ of the vibronic angular momentum,$^{[39]}$ $\langle G_z \rangle$,$^{[40]}

\begin{equation}
\zeta_1 = \zeta_d d_H + \langle G_z \rangle = \zeta_d d_H + \sum_i \zeta_i^2 \ell_i \tag{80}
\end{equation}

where $\zeta_i^2$ are the Coriolis coupling coefficients$^{[41,60]}$ which depend on the nature of the molecular vibrations. Comparison of the values of $\zeta_1$ and $\zeta_d d_H$ available from this and preceding studies shows that $\zeta_1$ is dominated by the electronic contribution and therefore its overall isotopic trend is expected to be also monotonic which is shown in Fig. 9 (blue triangles). However, the nature of the molecular vibrations changes substantially when the nuclear symmetry is reduced, which explains the deviations of the $\langle G_z \rangle$ from the monotonic trend for asymmetrically deuterated species, as is displayed in the right panel of Fig. 9. Since the vibrational angular momentum results from the interplay of multiple vibrational modes, the accurate calculations of the isotopic trends in $\zeta_d d$ and $\zeta_1$ would require very detailed information on the vibrational structure of the radicals, which is presently unavailable.

3. Rotational parameters $B_{xx}$, $B_{yy}$, $B_{zz}$, and $B_{xz}$

In the asymmetrically substituted species, the IAS (defined in Sec. III A) is not coincident with the principal axis system, which results in four rather than three non-vanishing rotational constants $B_{\alpha \beta}$. The experimentally obtained values of the rotational constants, $B_{\alpha \beta}$, are given in Table II. As discussed above and has been shown previously$^{[21,27]}$ the values of the $B_{\alpha \beta}$ contain both first ($X^1$) and second ($X^2$) order contribution, in which the latter can be further divided into electronic and vibrational parts, $X^2 = X^2_e + X^2_v$. Note that in this latter segregation the $X^2_v$ refers to terms arising from excited electronic states not effects within the electronic components of the ground state. $X^2_v$ refers to interactions with excited (from the ZPE levels) vibronic states in the ground state manifold. The first order contribution $X^1$ to the rotational constants $B_{xx}$, $B_{yy}$, $B_{zz}$ and $B_{xz}$ is the expectation value of the corresponding microscopic parameter of Eq. (26) in the basis of Eq. (17) of the ground vibronic state and is given by the first term, $B_{\alpha \beta}^{(1)}$, in in Eq. (30). The $B_{\alpha \beta}^{(1)}$ is dependent only on the details of the electronic potential, hence using the notation of Eq. (38) $B_{\alpha \beta}^{(1)} = B_{\alpha \beta}$. Since the electronic potential does not change with isotopic substitution, $B_{\alpha \beta}^{(1)}$ in all isotopologues is characterized by the same values of internal coordinates (i.e., bond lengths and angles) and the nuclear masses appropriate for each isotopologue, and therefore its value is directly related to molecular structural parameters.

The $B_{xx}$ and $B_{yy}$ rotational constants receive$^{[20]}$ a negligible second order Jahn-Teller contribution, $B_{xx}^{(2)}$ and $B_{yy}^{(2)}$ thus $B_{xx} = B_{xx}^{(1)}$ and $B_{yy} = B_{yy}^{(1)}$. It has been shown (see Table V of Ref. 20), however, that while the $B_{xx}$ rotational constant has a relatively small $B_{xx}^{(2)}$ contribution, it receives a substantial second order contribution due to vibronic interaction, $B_{xx}^{(2)}$, whose magnitude has been estimated previously$^{[27]}$. The dependence of $B_{xx}^{(2)}$ on symmetric isotopic substitution has been obtained$^{[21]}$ by the introduction of the common vibrational frequency scaling factor $B^f$ and the assumption that the electronic and vibrational integrals in Eq. (37) are not significantly affected by isotopic substitution as long as the nuclear symmetry is preserved. Therefore, it is possible to estimate the value of $B_{xx}^{(1)} = B_{xx}^f$ for the symmetric molecules. Having $B_{xx}^f$ available for all asymmetrically substituted species it is possible to obtain with substantial accuracy$^{[21]}$ their structural parameters, which are reproduced in Table VI.
TABLE VI. The magnitudes of the distortions $\delta_{ij}^{\alpha T}$ along $e$ (C$_{3v}$) vibrational modes $s_i$ in methoxy. These values are obtained from the fit of the experimentally observed values of $h_1$, $h_2$ of symmetric molecules studied previously, and $h_1$, $h_2$, $h'_1$, $h'_2$, and $h_B$ of the asymmetrically substituted molecules as described in the text. In the fit the values of all $h$-parameters are weighted inversely proportional to the squares of their experimental uncertainties. The fit values are compared to the results of ab initio calculations performed previously (columns 4 and 5). The structural parameters $R_{\text{CH}}$, $R_{\text{CO}}$, $R_{\text{CH}} - R_{\text{CD}}$, and $\theta_{\text{HOCO}}$ bond angle of the $R_2$ configuration of the conical intersection obtained previously are given in the bottom part of the table.

<table>
<thead>
<tr>
<th>Parameter $^a$</th>
<th>Fit</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>value</td>
<td>$1\sigma$</td>
</tr>
<tr>
<td>$\delta_{\text{Me-CO}}$ (deg)</td>
<td>4.2 (2)</td>
<td>4.05</td>
</tr>
<tr>
<td>$\delta_{\text{CH-Me-H'}}$ (deg)</td>
<td>2.9 (3)</td>
<td>1.7</td>
</tr>
<tr>
<td>$\delta_{\text{CH}}$ (mÅ)</td>
<td>25 (3)</td>
<td>2.8</td>
</tr>
<tr>
<td>$R_{\text{CO}}$ (Å)</td>
<td>1.36039 (8)</td>
<td>1.3934</td>
</tr>
<tr>
<td>$R_{\text{CH}}$ (Å)</td>
<td>1.10697 (9)</td>
<td>1.0892</td>
</tr>
<tr>
<td>$\theta_{\text{HOCO}}$ (deg)</td>
<td>111.65 (5)</td>
<td>109.98</td>
</tr>
</tbody>
</table>

The molecular distortion amplitudes $\delta_{\text{Me-CO}}$, $\delta_{\text{CH-Me-H'}}$, and $\delta_{\text{CH}}$, are related to the distortion parameters at the Jahn-Teller minimum (labeled “min”) and saddle point (“sp”) as follows: $\delta_{\text{Me-CO}} = (\delta_{\text{sp}} - \delta_{\text{min}})$, $\delta_{\text{CH}} = (\delta_{\text{sp}} - \delta_{\text{min}})$, $\delta_{\text{CH-Me-H'}} = (\delta_{\text{sp}} - \delta_{\text{min}})$, where $H$ is the hydrogen in xz-plane. The results of ab initio calculations report the deformation of the HCOH angle, which is equal to the difference between the angles of rotation of the planes containing C$_3$ and H and H' atoms, respectively. This results in the factor of $1/\sqrt{3}$ in the expression for $\delta_{\text{CH-Me-H'}}$. In terms of the $\psi_{\text{HOCO}}$ dihedral angles at saddle point and Jahn-Teller minimum.

$^a$Reference 61.
$^b$Reference 62.
$^c$The values of the structural parameters at the reference configuration are calculated in Ref. 58 using 6-311+G(2d,2p) basis set, except as noted.
$^d$Calculated using cc-pVTZ basis set.

In CH$_2$DO and CHD$_2$O, the effective values of $B_{zz}$ and $B_{zz}$, also receive a substantial second-order contribution due to the interaction with excited vibronic states. Unlike the symmetric case, however, neither of the two approximations that allow one to use Eqs. (39) and (40) hold anymore. Although for these reasons it is not feasible to estimate $B_{zz}^{(2o)}$ and $B_{zz}^{(2o)}$ accuracy sufficient for the quantitative structural analysis, the experimental values can be compared to the predictions of $B_{zz}^{sp}$ made by using the bond lengths and angles (see Table VI), and the appropriate nuclear masses. The resulting values are given in the “X1" column of Table II. Although the second order contribution to $B_{zz}$ and $B_{zz}$ are expected to be negligible (see Table V of Ref. 20), the comparison between the experimental and predicted values for these parameters shows discrepancies beyond the experimental errors. These discrepancies can be attributed to the effects of the higher order vibronic interactions or to Hamiltonian terms connecting the ground and excited vibronic states that have so far been neglected. Indeed, the ERH used in this analysis has been derived by reducing the rotational Hamiltonian using the transformation Eq. (20). This transformation only diagonalizes (and correctly accounts for the effects of the linear Jahn-Teller, but not the other vibronic interactions which may result in contributions to the vibrational constants.

For the purpose of crude estimates of $B_{zz}^{sp}$ and $B_{zz}^{sp}$ in CH$_2$DO and CHD$_2$O, we will use the parameter $B'$, Eq. (40) and approximate its value as the average of that in normal and perdeuterated species, $B' = 1.16$. Using Eqs. (37) and (39) we obtain the estimates of $B_{zz}^{(2o)}$ and $B_{zz}^{(2o)}$ which are given in Table II in the column labeled “X2.” The estimated values of the $X1 + X2$ for the corresponding rotational constants show reasonable agreement with the experimental results for the level of approximation used.

4. Rotational Jahn-Teller parameters $h_1$, $h_2$, $h'_1$, $h'_2$, $h_A$, and $h_B$

As Table II indicates, even the values of smaller of $h_1$, $h_2$, $h'_1$, $h'_2$, $h_A$, and $h_B$ parameters (or, for short, $h$-parameters) are experimentally determined to relatively good precision, for the most part to better than 10%. These parameters account for the rotational effects due to the dynamic Jahn-Teller distortion; hence the analysis of their values can potentially provide valuable information on the geometric distortion of the molecule. As Eqs. (35) and (36) of Sec. III A 3 show the effective rotational Hamiltonian, $H_{\text{ROT}}$, has six $h$ parameters. Each of the six parameters are defined, Eq. (36), in terms of linear combinations of derivatives of the elements of the rotational tensor, $B_{\alpha \beta}$, and $B'_{\alpha \beta}$, with respect to the mass weighted normal coordinates $q_j$, which transform respectively as $A'$ and $A''$ in the $C_{2i}$, symmetry of the asymmetrically deuterated molecule.

In the absence of a Jahn-Teller distortion all the $h$’s vanish. This can be seen directly from Eq. (36). For a linear Jahn-Teller effect the potential energy of the diatomic states can be expressed (see Eq. (10)) as a sum over $1/2k_m q_m^2 \pm k_m q_m$ for each normal mode $q_m$. Hence the coordinate $q_m$ at the distorted minimum is displaced from the conical intersection by an amount $\Delta q_m = k_m$. By Eq. (36) if all the $\Delta q_m = 0$, then all the corresponding $h$ parameters vanish.

For the asymmetrically substituted methoxy there are in principle 9 distortion parameters, $\Delta q_m$, one for each normal mode. However, the minimum number of parameters needed to describe the geometrics distortion is much smaller. In the symmetric molecule, the Jahn-Teller effect is restricted by symmetry to the 3 degenerate $e$ modes, each of which is characterized by a single distortion parameter, $q_i$. Since the distorted geometry is assumed not to change among the
isolated isotopologues, then 3 distortion parameters should suffice to describe this geometry.

Two conditions must be met to actually determine distortions from the experimental data. First Eq. (36) must be recast in terms of non-mass weighted symmetrized combinations of either Cartesian or internal coordinates, $s_i$. Such a linear transformation is straightforward,

$$q_i = \sum_j \left( \frac{\partial q_j}{\partial s_i} \right) s_i,$$

Substituting Eq. (81) into Eq. (36), we obtain for $B^\prime_{\alpha\beta}$,

$$B^\prime_{\alpha\beta} = -\sum_i k_i \left( \frac{\partial B_{\alpha\beta}}{\partial q_i} \right) - \sum_i \sum_j \left( \frac{\partial^2 B_{\alpha\beta}}{\partial q_i \partial q_j} \right) \Delta s^\prime_{iJT},$$

where $\Delta s^\prime_{iJT}$ is the the distortion along the internal coordinate from the conical intersection to the Jahn-Teller minimum, and $i$ runs over all modes of the appropriate symmetry. The expression for $B^\prime_{\alpha\beta}$ is similar. Since the $s_i$ are not mass-weighted, $\Delta s^\prime_{iJT}$ is iso-tropic-independent, and therefore their values are unchanged among isotopologues. The second requirement is that the derivatives, $(\partial B_{\alpha\beta}/\partial s_i)$, are obtained from a straightforward classical mechanics calculation. Numerical derivatives of the $B_{\alpha\beta}$ for each isotopologue are determined by calculating the $B_{\alpha\beta}$ for finite displacements of the $s_i$ from the reference configuration. It is then straightforward to combine this information with Eq. (35) to express the observed $h$ values as a function of the distorted equilibrium configuration of the $s^\prime_{iJT}$ or more directly their displacements $\Delta s_i$ from the reference configuration values.

The symmetrized internal coordinates that transform as the two components of the $e$ modes are expressed as linear combinations of the geometric parameters, $\theta_{Me-CO}$, $\varphi_{H-Me-H^*}$, and $r_{CH}$. As shown in Fig. 10, $\theta_{Me-CO}$ is the tilt angle between the methyl axis and C–O bond, $\varphi_{H-Me-H^*}$ is the “swing” amplitude of the HCO plane with respect to its position in undistorted configuration and $r_{CH}$ is the CH stretch. We define a set of displacements of the corresponding internal coordinates $\delta h_{Me-CO}^T$, $\delta \varphi_{H-Me-H^*}^T$, and $\delta r_{CH}^T$, as the radius of the circle (averaged for quadratic Jahn-Teller) of pseudo-rotation of each of the corresponding coordinates about its reference configuration value or equivalently half the differences in their value at the Jahn-Teller distorted global minima and the corresponding saddle-points around the moat.

One can now determine the best value for $\delta \theta_{Me-CO}$, $\delta \varphi_{H-Me-H^*}$, and $\delta r_{CH}$ by doing a least squares fit to the 18 observed $h$ values for the 5 isotopologues. When all 18 $h$ parameters are included, the quality of the fit was rather poor particularly with respect to the $h_A$ values. However it was recognized that the centrifugal distortion term for $\Delta E$ has precisely the same matrix elements in the $\hat{H}_G$ as does $h_A$, thus making it an effective parameter. Indeed rough estimates of the $\Delta E$ CD parameter indicates it would be comparable in magnitude to $h_A$ rendering the observed $h_A$ not a reliable structural parameter.

Our approach then was to eliminate the $h_A$ values from the still over-determined data set and fit the distortions, $\Delta s^\prime_{iJT}$. The values resulting from that fit are given in Table VI. Since $ab initio$ calculations have indicated that bilinear terms in the potential may be important, we also did fits where 3 displacements along internal coordinates transforming totally symmetrically were introduced in addition to the previous Jahn-Teller active, $e$ displacements. When these 6 parameters were fit to the remaining 16 $h$ value, none of the three symmetrical displacements were found significant within experimental error and the resulting Jahn-Teller displacements were essentially unchanged compared to experimental error. Ergo, based on the simple analytical model of the potential adopted we believe the values in Table VI represent the best geometric distortion values obtainable from the experimental data.

It is interesting to compare the “experimental geometry” (both at reference and distorted configurations) with quantum chemistry calculations. As shown in Table VI, one can see the computed and experimental values are qualitatively consistent, but there is considerable discrepancy between the experimental and theoretical values, as well as considerable discrepancy among the latter.

In making these comparisons it is important to note the possible shortcomings in each the experimental and computational result. The experimental result clearly assumes an over-simplified analytical model for the diabatic surfaces and vibronic coupling. It also could suffer from small, non-structural dependent contributions, like to $h_A$, to the remaining 16 $h$ parameters. In particular this could explain the large difference in the experimental and computed $\delta r_{CH}^T$, since it is expected to be very small, and even small contamination of the experimental value by non-structural contributions to the $h$’s could dramatically affect the derived value. On the theoretical side, it must be recognized that these are relatively small distortions which are challenging to capture accurately even with high-level calculations. On a more fundamental level, it must be remembered that the adiabatic potential and resulting theoretical distortion arises from a calculation that has neglected the coupling between the two nearly sheets of
the adiabatic potential. It is unclear what errors this neglect may introduce.

5. Spin-rotational coupling constant $\varepsilon_{zz}$

The majority of the spin-rotation parameters included in the ERH are defined by the second-order electronic contributions, $X^{(2v)}$, and are dynamically restricted in the fit. The exceptions to this rule are $\varepsilon_{zz}$ and $\varepsilon_{xz}$ which were shown earlier to be essentially defined by the second order vibronic contribution, $X^{(2v)}$. The $\varepsilon_{zz}$ and $\varepsilon_{xz}$ are related by Eq. (55) and hence only a single independent parameter, e.g., $\varepsilon_{zz}$, need to introduced in the fit with the value of $\varepsilon_{xz}$ being constrained to it via Eq. (55).

Similar to the case of the vibronic contributions to the rotational constants, e.g., $B_{zz}^{(2)}$, one can do a crude estimate of the value of $\varepsilon_{zz}$ using the isotopic relationships and the value of $B^I$, extrapolated to the partially deuterated species,

$$\varepsilon_{zz} = \varepsilon_{zz}^{CHD_2O} \frac{B^I_{zz}^{CHD_2O}}{B^I_{zz}^{CH_2DO}} \tag{83}$$

where $B^I_{zz}$ is the corresponding rotational constant of the protonated isotopologue. The predicted values of the $\varepsilon_{zz}$ for CH$_2$DO and CHD$_2$O are given in Table II.

Comparison of Eq. (83) and Eq. (39) shows that the $X^{(2v)}$ contributions to both $B_{zz}$ and $\varepsilon_{zz}$ exhibit the same dependence on $B^I$, and therefore, the corresponding experimental values should exhibit similar trends. In CH$_2$DO, the estimated value of $B_{zz}^{(2v)}$ gives a reasonably good agreement with the experiment; however, the magnitude of $\varepsilon_{zz}^{(2v)}$ is overestimated by about 6%. On the other hand, in CHD$_2$O the estimated value of $\varepsilon_{zz}^{(2v)}$ predicts the experimental value rather well, but $B_{zz}^{(2v)}$ is significantly underestimated. In part, these inconsistencies arise from the use of the same value of $B^I$ for both asymmetrically substituted species, since it is reasonable to suggest that its value should be greater for CHD$_2$O, as it tends to increase in heavier species. However, as in case of CD$_3$O, it is not possible to predict $B_{zz}^{(2v)}$ and $\varepsilon_{zz}$ simultaneously to the desired accuracy using $B^I$ as a vibrational scaling factor in Eqs. (39) and (83) for any given isotopologue. The comparison of $B_{zz}^{(2v)}$ and $\varepsilon_{zz}$ with the experimental values in all deuterated molecules shows that although $B^I$ can be used for predicting trends and rough numerical estimates, the accuracy of this simplified model is limited to about 10%.

B. Excited $\tilde{A}^2A_1$ electronic state

The $\tilde{A}$ state parameters resulting from fitting of the LIF spectra are given in Table III for the $3^3\Sigma$ band and in Table IV for the $6^3\tilde{g}_1$ band of both isotopologues. For the $3^3\Sigma$ band, the structural parameters are available from the studies of the symmetric species, therefore we predicted the values of the three rotational constants using previously derived bond lengths and angles. These values are given in the third column of the data subset of each of the two isotopologues in Table III. We note that although the agreement between the experimental and predicted values is somewhat poorer than for the ground state, the trends in the values of the rotational constants in $3^3\Sigma$ are predicted reasonably well. The observed rotational constants are functions of the expectation values of the structural parameters in the particular state, therefore moderate to small deviations of the experimentally observed values from the predicted ones, as well as a monotonic trend in the measured energies of the $3^3\Sigma$ level indicate that the character of the molecular motion in the $3^3\tilde{g}_1$ state is approximately the same in all four isotopologues for which this state has been measured.

The experimentally measured frequencies assigned to the $6^3\tilde{g}_1$ bands are somewhat surprising in that the energy of this level in CH$_2$DO is actually lower than that in CHD$_2$O. This observation can be qualitatively explained as follows. The $\nu_{8a}$ mode in CH$_2$DO and CHD$_2$O correlates with the symmetric component of the doubly degenerate methyl rock $\nu_b$ mode in the species with C$_3v$ symmetry, corresponding to the motion in $xz$-plane. If the rocking character is preserved, then the reduced mass associated with this motion in CH$_2$DO is expected to be smaller, and therefore, the frequency greater. On the other hand, if the character of this motion is dominated by the HCO bend, where H' is the in-plane hydrogen, which is substituted with deuterium in CH$_2$DO, the trend would be reversed. The latter scenario is observed experimentally which indicates that a substantial change in character of the methyl rock vibrational motion with a reduction of symmetry.

VI. CONCLUSIONS

High resolution spectra of a Jahn-Teller active molecule carry information on the details of the molecular potential energy surface and the vibronic interactions between the components of the degenerate electronic states. Due to its relatively simple molecular structure experimental measurements of the rotationally resolved spectra of the methoxy radical offer an opportunity to study these effects at a very high level of detail.

On the flipside, to describe the rotational spectra of these species to experimental accuracy requires development of a complex effective rotational Hamiltonian which makes the analysis challenging even in the case of the symmetric species. The reduction of nuclear symmetry complicates the situation even further by allowing additional terms to the vibronic Hamiltonian, and consequently, in the ERH.

In this work we have further extended the development of the ERH to allow us to consistently analyze high resolution spectra of both asymmetrically substituted methoxy radicals, CH$_2$DO and CHD$_2$O, to experimental accuracy, in the context of the knowledge obtained in the preceding studies of symmetric species. Despite the increased complexity of the ERH, we have shown that the application of various isotopic relationships allow us to simplify the numerical analysis and clarify the physical interpretation of the results even though the available data set for asymmetrically deuterated species is somewhat limited.

In terms of magnitude the largest of the parameters experimentally determined are the spin-orbit coupling, $a\tilde{c}_z$, and the splitting, $\Delta E$, of the zero-point vibronic degeneracy in the asymmetrically deuterated methoxies. We have demonstrated that quenching, $d_H$, of the spin-orbit coupling is a smooth and slowly varying function of the number of deuterons from 0
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to 3. For the first time a value of $\Delta E$ is derived from the observed vibronic splitting and is compared with its calculation via adiabatic eigenfunctions. The experimental value is found to be comparable to that obtained from the “best” calculations, but to be systematically somewhat larger.

Values for the rotational constants characteristic of the $C_3$ conical intersection configuration for the asymmetrically substituted methoxy are seen to be slightly different from those predicted from the geometric parameters obtained for the symmetric species. This is attributed to very small, non-geometric contributions to the effective rotational constants unique to the asymmetric species.

The Jahn-Teller induced geometric distortion of methoxy results in structurally dependent additions to the ERH characterized by several $h$ parameters. Analysis of these parameters yields an experimental measurement of this geometric distortion. When these experimental results are compared to calculated distortions, semi-quantitative, but certainly not exact agreement is found. It is unclear whether the remaining discrepancies is a result of short-comings in the relatively simple analytical potential used to analyze the experimental data or the calculated adiabatic wavefunctions (or both).

It has been found that nearly all the observed spin-rotation structure of the asymmetrically deuterated methoxy can be explained by spin-rotation tensor components derived from the symmetrical species using isotopic relations. The one exception is the experimentally determined $\epsilon_{zz}$ which is highly dependent upon vibronic interactions.

It is clear that the data set that is now available for 5 different isotopologues of methoxy represents a unique source for the study of a number of important molecular interactions such as spin-orbit coupling, vibronic degeneracy lifting, and Jahn-Teller geometric distortion. This data should serve to benchmark our understanding of these interactions for many years.

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APPENDIX A: QUENCHING PARAMETER FOR $H_{SO}$

This Appendix derives the quenching parameters for spin-orbit coupling, $d_{H}$, in the multimode case. We first expand the expression for the microscopic Hamiltonian Eq. (19) using the expression,

$$\hat{H} = e^{i\hat{\mathcal{S}}} H e^{-i\hat{\mathcal{S}}} = H + i[\mathcal{S}, H] + \frac{1}{2} [\mathcal{S}, [H, \mathcal{S}]] + \ldots$$

(A1)

$H_{SO}$ contains no vibrational coordinates, and $H_{A}$ contains only squares of vibrational coordinates $\mathbf{q}$ and momenta $\mathbf{p}$, and $\mathcal{S}$ only contains $p$ in first power. Both $\mathbf{q}$ and $\mathbf{p}$ act as raising and lowering operators, therefore it is evident that the second term in the right hand side of Eq. (A1) contains only odd powers of $\mathbf{q}$ and has no nonvanishing matrix elements within the ground vibronic twofold, and will be ignored. To evaluate the last term in Eq. (A1), we note that $\mathcal{S}$ has form of

$$\mathcal{S} = \begin{pmatrix} 0 & \hat{a} - i\hat{b} \\ \hat{a} + i\hat{b} & 0 \end{pmatrix},$$

(A2)

where

$$\hat{a} = \sum_{s} k_{s} p_{s},$$

$$\hat{b} = \sum_{t} k_{t} p_{t},$$

(A3)

and index $s$ runs over $A'$ vibrational modes and $t$ runs over $A''$ vibrational modes. Substituting the matrix expression for the spin-orbit Hamiltonian $H_{SO}$ in the $|e_{\pm}\rangle$ basis,

$$H_{SO} = a \zeta_{e} \Sigma \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(A4)

and the expression for $\mathcal{S}$ in Eq. (A1), we obtain

$$\hat{H}_{SO} = H_{SO} + \frac{1}{2} [\mathcal{S}, [H_{SO}, \mathcal{S}]] = a \zeta_{e} \Sigma \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$+ \frac{1}{2} a \zeta_{e} \Sigma \begin{pmatrix} -4(\hat{a}^{2} + \hat{b}^{2}) & 0 \\ 0 & 4(\hat{a}^{2} + \hat{b}^{2}) \end{pmatrix},$$

(A5)

All operators $\hat{a}$ and $\hat{b}$ commute with each other; therefore the off-diagonal elements in Eq. (A5) vanish. The operators $\hat{a}^{2}$ and $\hat{b}^{2}$ are the sums of terms quadratic and bilinear in $p$, of which only quadratic terms produce nonvanishing matrix elements within the ground vibronic twofold, e.g.,

$$\langle v = 0 | \sum_{s} k_{s} p_{s} \sum_{s'} k_{s'} p_{s'} | v = 0 \rangle = \langle v = 0 | \sum_{s} k_{s}^{2} p_{s}^{2} | v = 0 \rangle$$

$$= \frac{1}{2} \sum_{s} k_{s}^{2}.$$ (A6)

Substituting the expression Eq. (A6) for $\hat{a}^{2}$ and $\hat{b}^{2}$ into Eq. (A5), we obtain

$$\hat{H}_{SO} = a \zeta_{e} \Sigma \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$+ a \zeta_{e} \Sigma \begin{pmatrix} -\frac{1}{2} \sum_{s} k_{s}^{2} - \sum_{t} k_{t}^{2} & 0 \\ 0 & \frac{1}{2} \sum_{s} k_{s}^{2} + \sum_{t} k_{t}^{2} \end{pmatrix}$$

$$= a \zeta_{e} \Sigma d_{H} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$ (A7)
where \( d_H = 1 - \sum_i k_i^2 = \sum_i k_i^2 \). In a symmetric molecule, \( k_s = 0 \) for the totally symmetric \((A_1)\) modes. Using Watson’s convention to relabel the components of the doubly degenerate modes, \( s = ma, t = mb, \) and \( k_{ma} = k_{mb} = k_m \), we obtain

\[
d_H = d_{1/2,0} = \left(1 - 2 \sum_m k_m^2 \right) = \left(1 - 4 \sum_m D_m \right),
\]

(A8)

where in last equality \( k_m \) is recast in terms of linear Jahn-Teller parameter, \( 2D_m = k_m^2 \) and reduced to a previously obtained result.\(^6^4\)

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**APPENDIX B: OPERATOR FORM AND MATRIX ELEMENTS FOR TERMS IN THE ERH INTRODUCED BY ASYMMETRY**

1. Rotational terms \( h'_1, h'_2, h_A, \) and \( h_B \)

The rotational part of ERH of the asymmetrically substituted methoxy radicals is given in Eq. (33). The new terms accounting for the asymmetry-induced effects of Jahn-Teller distortion are given in the last two lines of this equation and are summarized as \( \tilde{H}_\text{ROT}^A \):

\[
\tilde{H}_\text{ROT}^A = h'_1(L^2 N_2^2 + L^2 N_2^2) + h'_2(L^2 N_2^2 + L^2 N_2^2) + h_A N_2^2(L^2 + L^2)
\]

(B1)

The matrix elements of \( \tilde{H}_\text{ROT}^A \) are given as follows:

\[
\left\{ J, -(P + 2), S, \Sigma' = \frac{1}{2}, \pm \right| h'_1(L^2 N_2^2 + L^2 N_2^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \pm (-1)^{J-P+\Sigma-2} h'_1 \sqrt{J(J+1)} - P(P+1) \sqrt{J(J+1) - (P+1)(P+2)},
\]

(B2)

\[
\left\{ J, -(P + 1), S, \Sigma' = \frac{1}{2}, \pm \right| h'_2(L^2 N_2^2 + L^2 N_2^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \mp (-1)^{J-P+\Sigma} 2 h'_2 \sqrt{J(J+1) - P(P+1)},
\]

(B3)

\[
\left\{ J, -P, S, \Sigma' = -\frac{1}{2}, \pm \right| h_A N_2^2(L^2 + L^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \pm (-1)^{J-P+\Sigma} 2 h_A P,
\]

(B4)

\[
\left\{ J, -P, S, \Sigma' = \frac{1}{2}, \pm \right| h_A N_2^2(L^2 + L^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \pm (-1)^{J-P+\Sigma} h_A (P - \Sigma)^2,
\]

(B5)

\[
\left\{ J, -(P-1), S, \Sigma' = \frac{1}{2}, \pm \right| h_B N_2^2(L^2 + L^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \pm (-1)^{J-P+\Sigma} 2 h_B (2J(J+1) - 2P^2 + 1),
\]

(B6)

\[
\left\{ J, -(P+1), S, \Sigma' = \frac{1}{2}, \pm \right| h_B N_2^2(L^2 + L^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \mp (-1)^{J-P+\Sigma} 2 h_B \sqrt{J(J+1) - P(P+1)},
\]

(B7)

\[
\left\{ J, -(P+1), S, \Sigma' = \frac{1}{2}, \pm \right| h_B N_2^2(L^2 + L^2) \right| J, P, S, \Sigma = -\frac{1}{2}, \pm \right) = \mp (-1)^{J-P+\Sigma} 2 h_B \sqrt{J(J+1) - P(P+1)}.
\]

(B8)
2. Spin-rotational terms $\varepsilon_{1a}', \varepsilon_{1b}', \varepsilon_{2a}', \varepsilon_{2b}',$ and $\varepsilon''$

The spin-rotational terms in the ERH of the asymmetrically substituted methoxy radicals arising from the effects of Jahn-Teller distortion are given in Eq. (48). The last five terms in the latter equation account for the asymmetry effects and can be summarized as $\tilde{H}_{\text{SR}}^A$:

$$\tilde{H}_{\text{SR}}^A = \varepsilon_{1a}'(\mathcal{L}^2_2 + \mathcal{L}^2_{-2})N_zS_z + \varepsilon_{2a}'(\mathcal{L}^2_2[N_+ N_-]_+ + \mathcal{L}^2_{-2}[N_+ N_-]_+)$$

$+$ $\varepsilon_{1b}'(\mathcal{L}^2_2[N_+ N_-]_+ + \mathcal{L}^2_{-2}[N_+ N_-]_+)$

$+$ $\varepsilon_{2b}'(\mathcal{L}^2_2[N_+ N_-]_+ + \mathcal{L}^2_{-2}[N_+ N_-]_+)$

$+$ $\varepsilon''(\mathcal{L}^2_2[N_+ N_-]_+ + \mathcal{L}^2_{-2}[N_+ N_-]_+)$.

(B10)

Therefore, the matrix elements of $\tilde{H}_{\text{SR}}^A$ are given in the following equations:

$$\left\langle J, -P, S, \Sigma' \right| \varepsilon_{1a}'(\mathcal{L}^2_2 + \mathcal{L}^2_{-2})N_zS_z \left| J, P, S, \Sigma = \frac{1}{2}, \pm \right\rangle = \pm (-1)^{J-P+S-\Sigma} \varepsilon_{1a}' \Sigma P,$$

(B11)

$$\left\langle J, -P, S, \Sigma' = \frac{1}{2}, \pm \right| \varepsilon_{2a}'(\mathcal{L}^2_2[S_- N_+]_+ + \mathcal{L}^2_{-2}[S_+ N_-]_+) \left| J, P, S, \Sigma = \frac{1}{2}, \pm \right\rangle = \mp (-1)^{J-P+S-\Sigma} 2\varepsilon_{2a}' P,$$

(B12)

$$\left\langle J, -(P+1), S, \Sigma' = \frac{1}{2}, \pm \right| \varepsilon_{1b}'(\mathcal{L}^2_2[S_- N_+]_+ + \mathcal{L}^2_{-2}[S_+ N_-]_+) \left| J, P, S, \Sigma = \frac{1}{2}, \pm \right\rangle = \pm (-1)^{J-P+S-\Sigma} \varepsilon_{1b}' \sqrt{J(J+1) - P(P+1)},$$

(B13)

$$\left\langle J, -(P-1), S, \Sigma' = \frac{1}{2}, \pm \right| \varepsilon_{2b}'(\mathcal{L}^2_2[S_- N_+]_+ + \mathcal{L}^2_{-2}[S_+ N_-]_+) \left| J, P, S, \Sigma = \frac{1}{2}, \pm \right\rangle = \pm (-1)^{J-P+S-\Sigma} \varepsilon_{2b}' \sqrt{J(J+1) - P(P-1)},$$

(B14)

$$\left\langle J, -(P+1), S, \Sigma' = \frac{1}{2}, \pm \right| \varepsilon''(\mathcal{L}^2_2[N_+ N_+]_+ + \mathcal{L}^2_{-2}[N_+ N_-]_+) \left| J, P, S, \Sigma = \frac{1}{2}, \pm \right\rangle = \pm (-1)^{J-P+S-\Sigma} 2\varepsilon'' \sqrt{J(J+1) - P(P+1)},$$

(B15)